INVESTIGATIONS INTO THE SYNTHESIS AND PROPERTIES OF INDENOPYRIDINES

BY

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I am indebted to my supervisors, Dr J Braven and Dr R W Hanson for their advice, support and encouragement throughout the programme of research.

I would also like to thank Key Organics Ltd. who kindly donated 3-methyl-2-phenylpyridine and two substituted hydroxylamines.

A special thanks to my father, mother and Mel who gave me continual support and encouragement over the course of the research programme.

Declaration

The synthetic work described herein is the original work of the author, except where acknowledgement is made by reference, and was carried out in the Department of Environmental Sciences at the University of Plymouth.

The work contained within this thesis has not been submitted for any other degree or award.

A series of related studies has been carried out throughout the research programme, these include

- regular attendance at the Royal Society of Chemistry meetings
- a short course on mass spectrometry, 'Interpretation of mass spectra' , UMIST , 1989.
- two conferences , 'Progress in Natural Product Chemistry' University of Nottingham , 1988 and 'Modern Aspects of Heterocyclic Chemistry', University of Nottingham, 1990.
- visits to Schering Agrochemicals Ltd. Chesterford Park Research Station , Saffron Walden and Key Orgenics , Camelford , Cornwall .

A Sugden

April 1993

INVESTIGATIONS INTO THE SYNTHESIS AND PROPERTIES OF INDENOPYRIDINES.

By Angela Sugden April 1993.

Abstract

Two novel routes have been investigated.Cyclisation of enamidoindenes by the Vilsmeier-Haack formylation was not possible because the condensation between indanones and acetamide,under acidic conditions, did not afford the desired monomer but instead two dimers,reported previously, were observed.The two routes by which these dimers maybe formed were thoroughly investigated and led to the synthesis of three novel compounds and a known compound, trùxene.

Omission of an acid catalyst afforded 2-acetamidoindene but not 1-acetamidoindene.

Since commercial 2-indanone was found to be impure by TLC and melting point,a sample was synthesised using a literature method. Pure 2-indanone failed to react with acetamide. It seemed that 2-acetamidoindene was produced via an impurity in commercial 2-indanone and then only in poor yield. Attempts to identify the impurity were unsuccessful.

The thermolytic Wolff rearrangement of benz[h]quinoline-5,6-diazoketone to benzyl 5H-indeno[1,2-b]pyridine-5-carboxylate initially proved promising.Many products were observed but none were isolated in sufficient purity for spectral characterisation.

The photolytic Wolff rearrangement of 9-diazo-10-phenanthrone gave 9H-fluorene-9N-tertbutylcarboxamide whose physical properties,which were previously unknown,were recorded. Rearrangement of the pyridyl analogue appeared promising. Spectroscopic data indicated the desired products, but isolation of pure compounds was not achieved.

Using a published synthesis, 5H-indeno[1,2-b]pyridin-5-one was made and reduction,by two separate methods,afforded the methylene compound.From these starting materials twenty-two novel compounds were made.For example, reduction of the ketone afforded the known alcohol (RS)5-hydroxy-5H-indeno [1,2-b] pyridine.Grignard reaction afforded the novel compound 5-hydroxy-5-phenylindeno [1,2-b] pyridine.

The two substituted oximes, 5H-indeno[1,2-b]pyridin-5-one 2-chlorobenzyloxime and 2,4-dichlorobenzyloxime were prepared.Reduction of the known 5H-indeno[1,2-b]pyridin-5-one oxime afforded 5-acetamido-5H-indeno[1,2-b]pyridine. Substitution reactions afforded the known 7-bromo- and 7,9-dibromo-5H-indeno[1,2-b]pyridin-5-one. Dibromo- and tribromo-5H-indeno[1,2-b]pyridine were prepared,as confirmed by mass spectrometry.The novel 6,7,8,9-tetrabromo-5H-indeno [1,2-b]pyridine was obtained pure and fully characterised. The nitro- derivatives of the ketone and methylene compounds were prepared. Reduction of these compounds afforded the amino- derivatives which were diazotised to give the corresponding hydroxy- derivatives.
Novel oximes of the 7-bromo- and 7-nitro-5H-indeno[1,2-b]-pyridin-5-one derivatives were synthesized and then reduced to the corresponding 5-acetamido- derivatives.
7-nitro-5H-indeno[1,2-b]pyridin-5-one when reduced,gave the unexpected 5,7-diacetamido- derivative. 7-acetamido-5H-indeno[1,2-b]pyridin-5-one was also prepared.
The known N-oxides of the ketone and methylene compounds were produced, as well as the novel N-oxides of the nitro-derivatives of 5H-indeno[1,2-b]pyridin-5-one and 5H-indeno [1,2-b]pyridine.

From fluorene, 9-butyl, 9-propyl and 9-phenyl-9-hydroxy-fluorene were prepared by Grignard reaction.Reduction of fluorenone using triethylsilane gave, unexpectedly, 9,9'-bifluorenyl.

The structures of known and novel compounds were confirmed by spectroscopic methods including ^{13}C , ^{1}H NMR ,infrared spectroscopy, mass spectrometry, melting point and TLC.

Contents

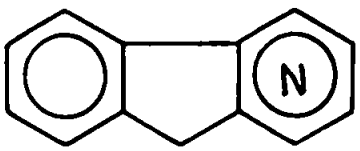
Appendices.

List of Abbreviations.

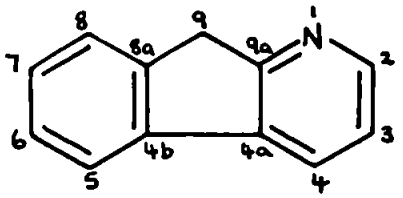
THF	tetrahydrofuran
RBF	round bottomed flask
TLC	thin layer chromatography
NBS	N-bromosuccinamide
NMR	nuclear magnetic resonance
IR	infrared
MS	mass spectrometry
DCM	dichloromethane
NaOH	sodium hydroxide
$MgSO_4$	magnesium sulphate
H_2SO_4	sulphuric acid

Chapter 1. Nomenclature of Indenopyridines.

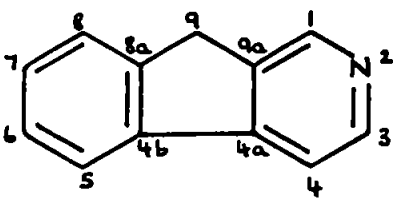
Indenopyridines, whose general structure is shown below, are tricyclic fused nitrogen-containing systems.



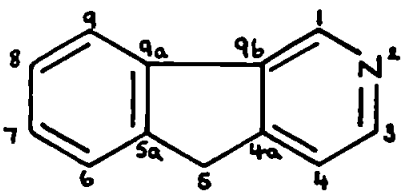
The position of the nitrogen atom in the pyridine ring varies to provide 4 isomers as shown below (trivial names in parentheses).



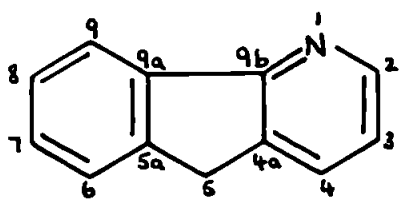
(1) 9H-indeno[2,1-b]pyridine (1-azafluorene)



(2) 9H-indeno[2,1-c]pyridine (2-azafluorene)



(3) 5H-indeno[1,2-c]pyridine (3-azafluorene)

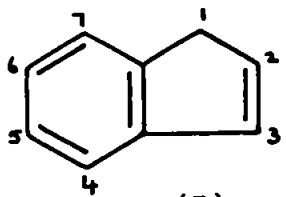


(4) 5H-indeno[1,2-b]pyridine (4-azafluorene)

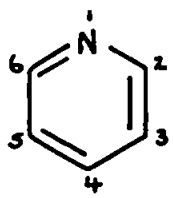
The indenopyridine ring system can be described using two systems of nomenclature.

1. Using trivial nomenclature fluorene is considered to be the parent; the position of the nitrogen atom is indicated by the locant number.In each case, the series of locant numbers starts in the pyridyl ring and terminates at the methylene bridge; the numbering system is analogous to that used for fluorene.

2. An alternative systematic approach to the nomenclature of the indenopyridine ring system is based on the fusion method.[1] The identifiable components of the system are indene (**5**) and pyridine (**6**).



(5)



(6)

The relevent IUPAC rule[2] on nomenclature indicates that the heterocyclic moiety takes precedence over the indene moiety as the base component, leading to the name indenopyridine.

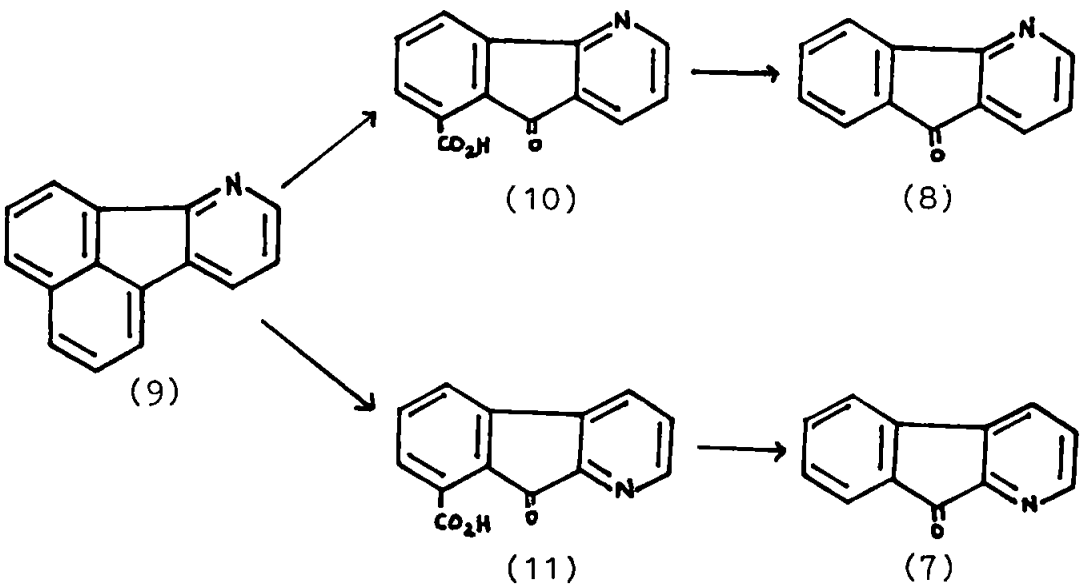
For each isomer, the ring junction is specified in pyridine by the use of the letters a,b or c, corresponding to the 1,2 2,3 or 3,4 bonds (all relative to the nitrogen atom). Junctions in the indene component are indicated using the numbering system approved by I.U.P.A.C.

A fusion site between the attached component and the base component can then be specified by placing the appropriate numbers and letters (separated by a hyphen) inside square brackets between the attached and base components.
Using this system 4-azafluorene (4) is named as 5H-indeno[1,2-b]pyridine.
Although the trivial name , azafluorene, is still widely used in the literature, the fusion system of nomenclature will be used throughout this thesis, as illustrated on page 1.

Chapter 2. Historical.

The earliest reported synthesis of an indenopyridine appears in 1883 when Skraup and Coblenz[3] obtained 9H-indeno[2,1-b]pyridin-9-one (7) and 5H-indeno[1,2-b]-pyridin-5-one (8) by the oxidation of benz[f]quinoline and benz[h]quinoline respectively.

In 1948 , Kruber and Rappen[4] noted the presence of an indenopyridine in coal tar distillates. They isolated and identified 5H-indeno[1,2-b]pyridin-5-one (8) as a component of the quinoline base fraction of anthracene coal tar. Oberkobusch[5] isolated 10-azafluoranthene (9) by distillation from coal tar pitch and oxidised it with potassium permanganate to obtain a mixture of 5H-indeno[1,2-b]pyridin-5-one-6-carboxylic acid (10) and 9H-indeno[2,1-b]pyridin-9-one-8-carboxylic acid (11) ; subsequent decarboxylation gave the corresponding indenopyridones (8) and (7) repectively .Scheme 1.



Scheme 1

In recent years, reports have appeared identifying 5H-indeno[1,2-b]pyridin-5-one (8) and 5H-indeno[1,2-b]-pyridine (4) in the environment. Examples are the atmosphere[6], lake sediments[7], shale and Iranian crude oil[8], Anthracene oil (basic fraction)[9] and cigarette smoke condensate[10].
A search of the literature indicates that none of the 9-isomers have been identified in the environment.
The main source of indenopyridine compounds in the environment are those associated with the combustion and processing of those fossil fuels which possess a high concentration of nitrogenous compounds.
5H-Indeno[1,2-b]pyridine-5-one (8) was never considered to be a naturally occurring compound until it was isolated from Onychopetalum amazonicum by deAlmeida[11] in 1976.
Since this date several naturally occurring indenopyridines have been isolated and identified, their structures being based on the 5H-indeno[1,2-b]pyridin-5-one 'skeleton' ; these are the subject of Chapter 5.

Chapter 3. Reactions and Properties of Indenopyridines.

Of the isomeric indenopyridines, 9H-indeno[2,1-c]pyridine (2) has been the most thoroughly studied. 5H-indeno[1,2-b]pyridine (4) and 5H-indeno[1,2-c]pyridine (3) have received very little attention in the chemical literature.

The reactions of indenopyridines and indenopyridones can be grouped into four main areas -

a. Electrophilic Aromatic Substitution in the homonuclear ring.
b. Reactions in the heterocyclic ring.
c. Reactions of the methylene group.
d. Reactions of an oxo group at the bridge carbon.

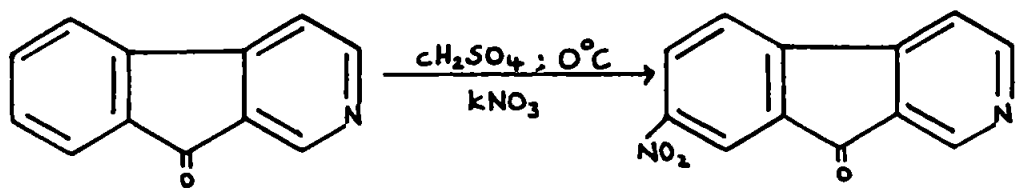
As with fluorene and it's derivatives , area d has received most attention.

a. Electrophilic Substitution in the Homonuclear ring.

Several workers [12,13,14,15] have prepared nitro- and halogen derivatives of indenopyridines.

1. Nitration.

The nitration of 9H-indeno[2,1-c]pyridin-9-one (12) by Périn-Roussel and Jacquingnon gave the 7-nitro compound in 70% yield.[13] Scheme 2.

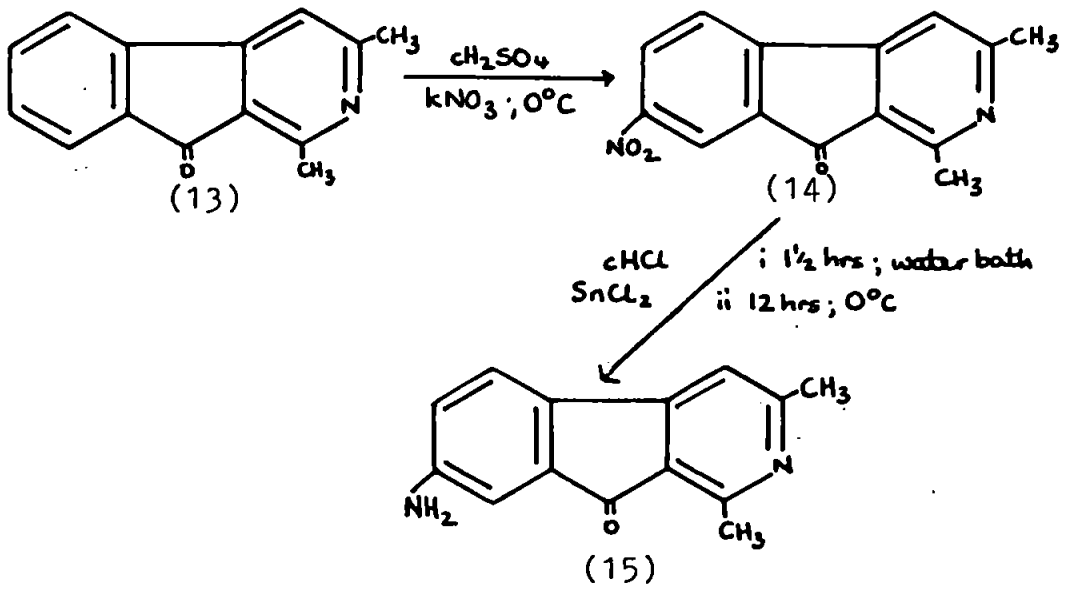


(12)

Scheme 2

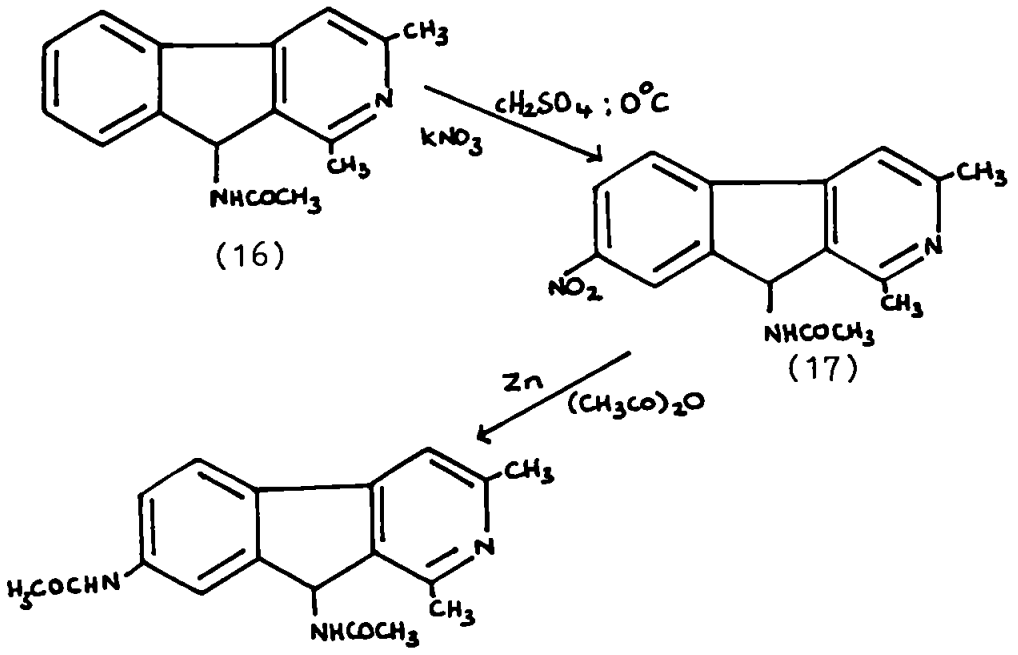
The nitration of 1,3-dimethyl-9H-indeno[2,1-c]pyridin-9-one (13) gave a good yield of a mono nitro- derivative[12] (14). From analogy with the formation of 2-nitrofluorenone from fluorenone by nitration under comparable conditions , compound (14) was named 1,3-dimethyl-7-nitro-9H-indeno[2,1-c] pyridin-9-one (14).

Reduction of the 7-nitro- compound (14) gave the 7-amino- compound (15) , in good yield .Scheme 3.



Scheme 3

Kahn et al[14] have nitrated 9-acetamido-1,3-dimethyl-9H-indeno[2,1-c]pyridine (16) to afford the 7-nitro - derivative (17) in good yield.Reduction of (17) with zinc dust in acetic anhydride yielded 7,9-diacetamido-1,3-dimethyl-9H-indeno[2,1-c]pyridine (18).Scheme 4.

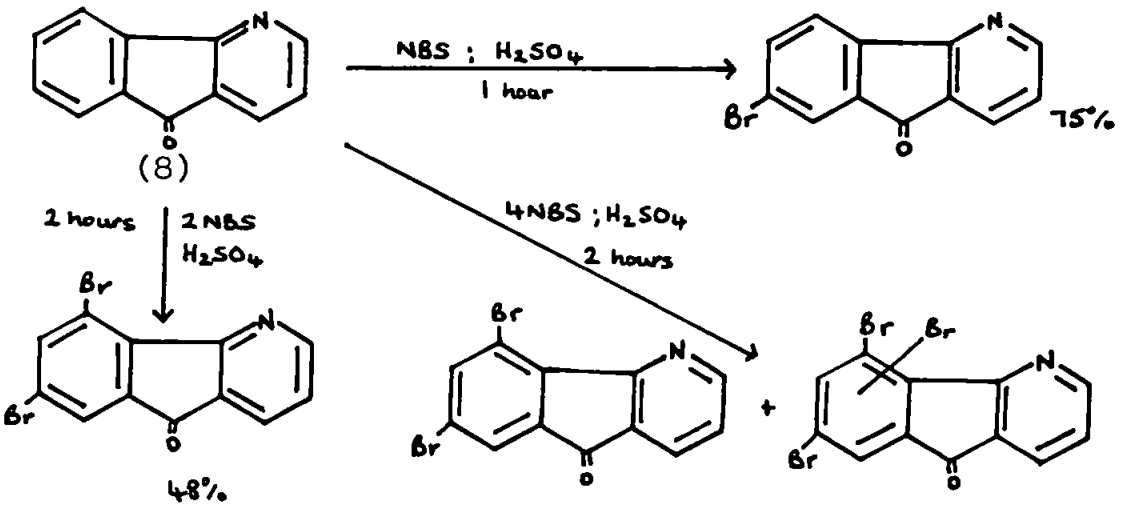


Scheme 4

There have been no reports of the nitration of the hydrocarbon compound - 9H-indeno[2,1-c]pyridine (2).

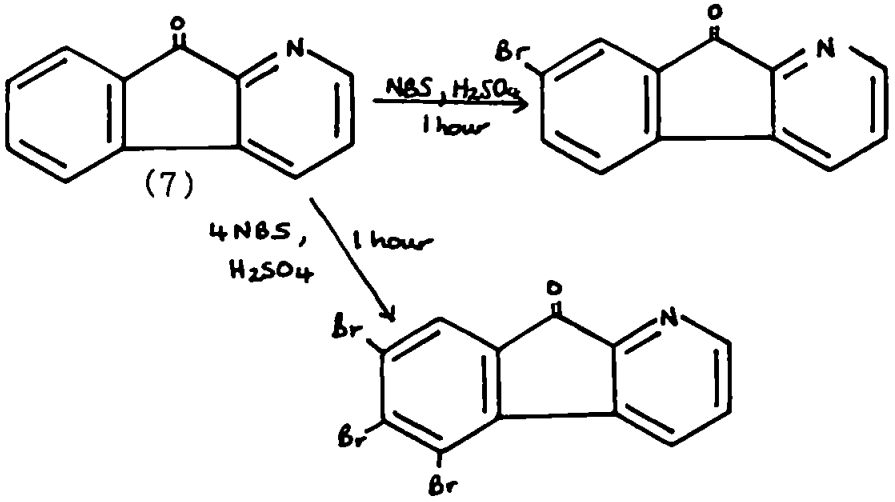
2. Halogenation.

Mlochowski and Szulc[15] have prepared several bromo-derivatives.Reaction of 5H-indeno[1,2-b]pyridin-5-one (8) with N-bromosuccinimide (NBS) in a 1:1 ratio afforded the mono-bromo derivative. Under more vigorous conditions the dibromo- and tribromo- derivatives were obtained.Scheme 5.



Scheme 5

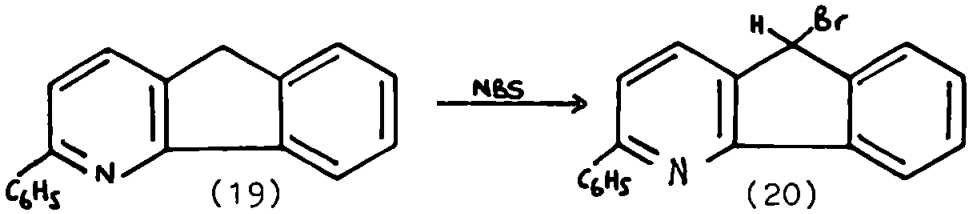
With 9H-indeno[2,1-b]pyridin-9-one (7), the monobromo-derivative was obtained in 53% yield, the tribromo-derivative in 64% yield (Scheme 6)



Scheme 6

When a single substituent ($-NO_2$, -Br) enters an indenopyridone compound, it substitutes at the C-7 position.There have been no reports of nitration or halogenation of the corresponding indenopyridines. There is little evidence of direct bromination of the methylene compounds in the literature. Mlochowski and Szulc[15] only obtained 7-bromo-5H-indeno[1,2-b]pyridine by reduction of the 7-bromo-5H-indeno[1,2-b]pyridin-5-one compound.

Pavel et al[16], however, reacted 2-phenyl-5H-indeno[1,2-b]-pyridine (19) with NBS to afford 2-phenyl-5-bromo-5H-indeno[1,2-b]pyridine (20) in 31% yield.Scheme 7.



Scheme 7

In this case , the bromo- substituent enters at the methylene position.

This appears to be the only report of direct halogenation of a 5H-indeno[1,2-b]pyridine in the literature.

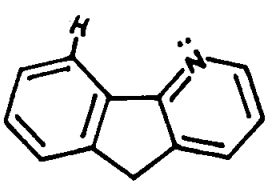
A search of the literature also reveals that there is no report of the halogenation of indenopyridines or indenopyridones, occurring in the pyridine ring.

b. Reactions in the Heterocyclic ring.

The main reports concerning reactions of the heterocyclic ring are associated with the derivatisation of the pyridyl nitrogen atom , eg. N-oxidation and N-alkylation.

Kloc et al[17] and Prostakov[18] studied N-methylation of 9H-indeno[2,1-b]pyridine (1), 5H-indeno[1,2-b]pyridine (4) and their corresponding oxo derivatives (7 ,8).

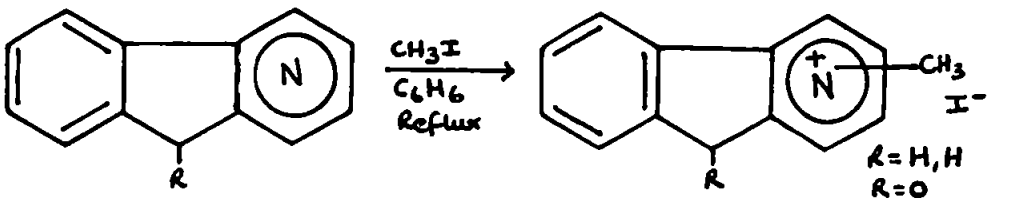
They found that (4) was less nucleophilic than expected, due to the effect of steric hindrance from the proton on C-9 to the lone pair of electrons on the pyridyl nitrogen, as indicated by the more accurate representation of (4).



(4)

Mlochowski and Szulc [15], whilst studying the rate of N-methylation of these compounds, also found that the indenopyridines are more reactive to N-methylation than their oxo derivatives.

Kloc and coworkers [17] also prepared the N-methyl derivatives of indenopyridines and their oxo derivatives. Scheme 8.



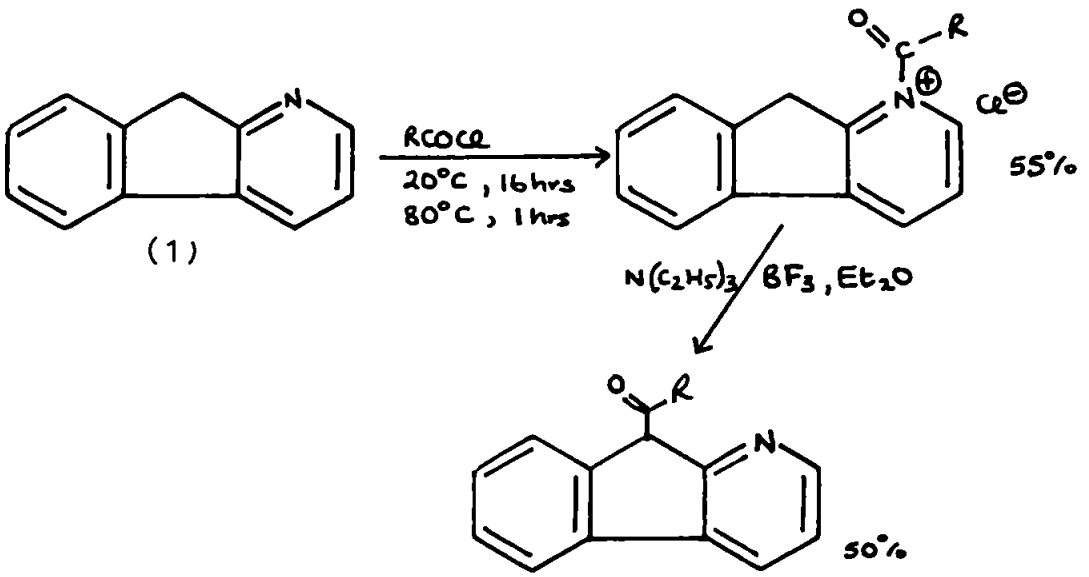
Scheme 8

Kloc et al [17] also found that the indenopyridines were more reactive than their corresponding indenopyridones, to N-methylation, as shown in Table 1.

No	Compound	Relative Rate
4	5H-indeno[1,2-b]pyridine	19
8	5H-indeno[1,2-b]pyridin-5-one	1
1	9H-indeno[2,1-b]pyridine	17
7	9H-indeno[2,1-b]pyridin-9-one	1

Table 1. Relative rate of N-methylation.

Prostakov [19] has reported a reaction involving the conversion of the N-acetyl and N-benzoyl derivatives of 9H-indeno[2,1-b]pyridine (1) to the corresponding 9-acetyl and 9-benzoyl compounds (21 and 22 respectively) by treatment with triethylamine and borontrifluoride etherate. Scheme 9.



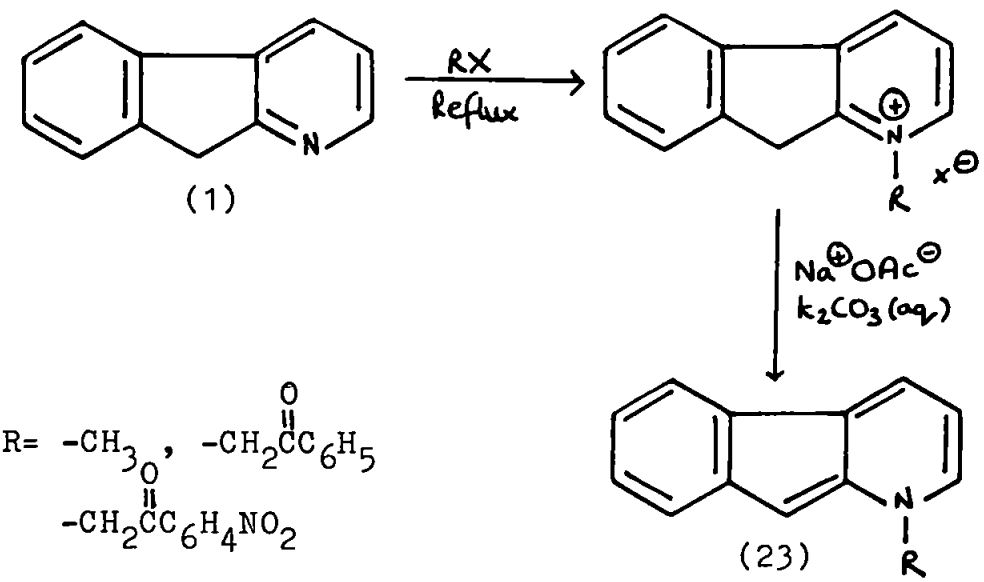
(1)

R=CH_3 (21)

R=$CH_2C_6H_5$ (22)

Scheme 9

Prostakov et al, [19,20] have also shown that N-methyl, N-phenacyl and N-(4-nitrophenacyl) derivatives of (1) can be converted, via the intermediate pyridinium salts, into the 1-H compounds (23) which have been described as pseudoazulenes.Scheme 10.



(1)

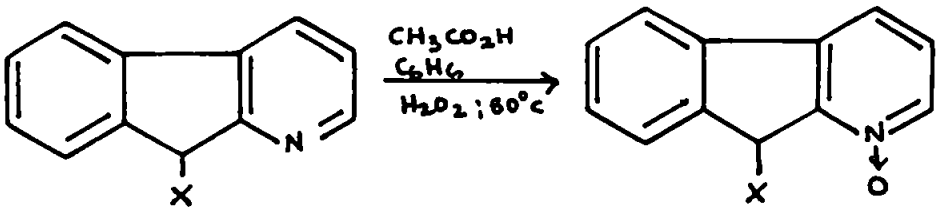
R= $-CH_3$, $-CH_2\overset{O}{\overset{\|}{C}}C_6H_5$, $-CH_2\overset{O}{\overset{\|}{C}}C_6H_4NO_2$

X=I,Br

(23)

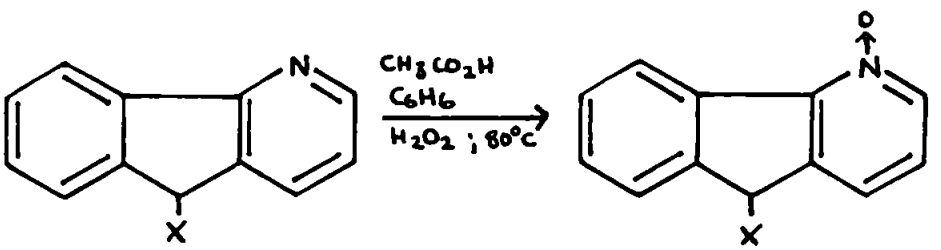
Scheme 10

Kloc et al[17] have oxidised indenopyridines and indenopyridones to their corresponding N-oxides with hydrogen peroxide in acetic acid .Scheme 11



X=O (7) X=O (69%)

X=H_2(1) X=H_2(54%)

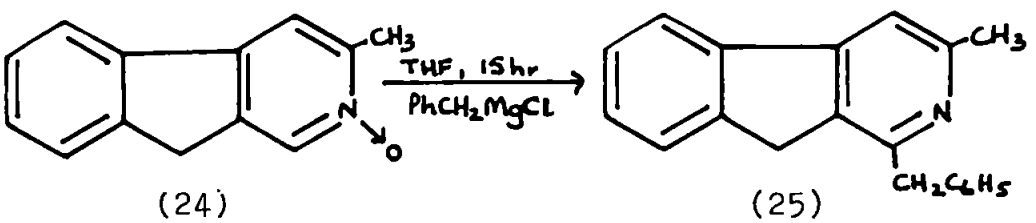


X=O (8) X=O (68%)

X=H_2(4) X=H_2(45%)

Scheme 11

Prostakov[21] used 3-methyl-9H-indeno[2,1-c]pyridine N-oxide (24) with benzyl-magnesium chloride to afford 1-benzyl-3-methyl-9H-indeno[2,1-c]pyridine (25).Scheme 12.

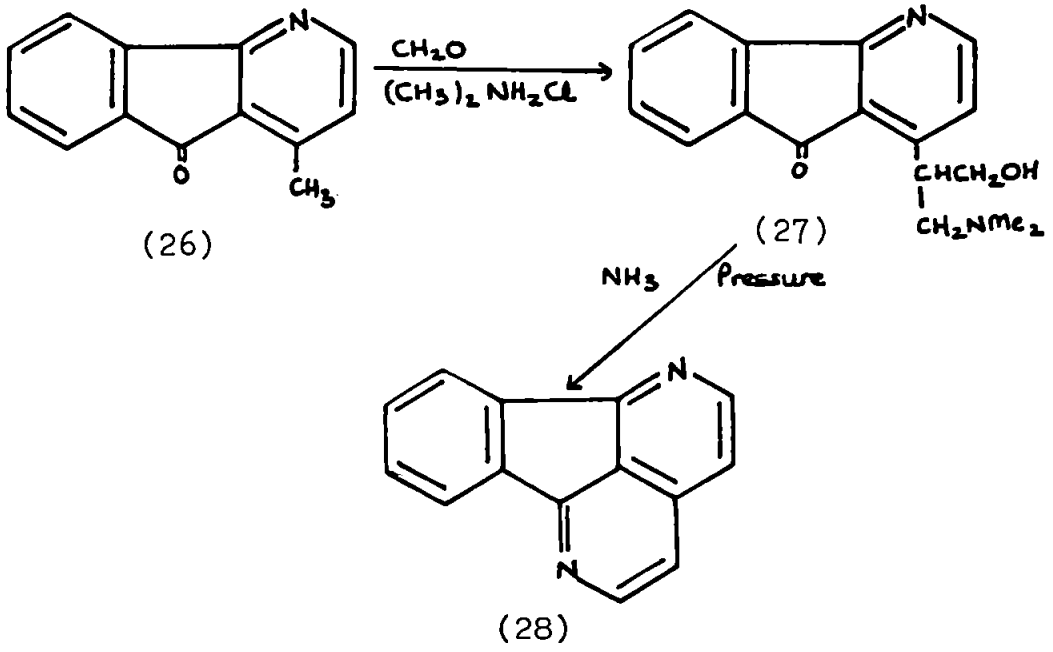


(24) (25)

Scheme 12

Treatment of 4-methyl-5H-indeno[1,2-b]pyridin-5-one (26) with formaldehyde and dimethylammonium chloride by Bowden et al[22] yielded the Mannich product (27).

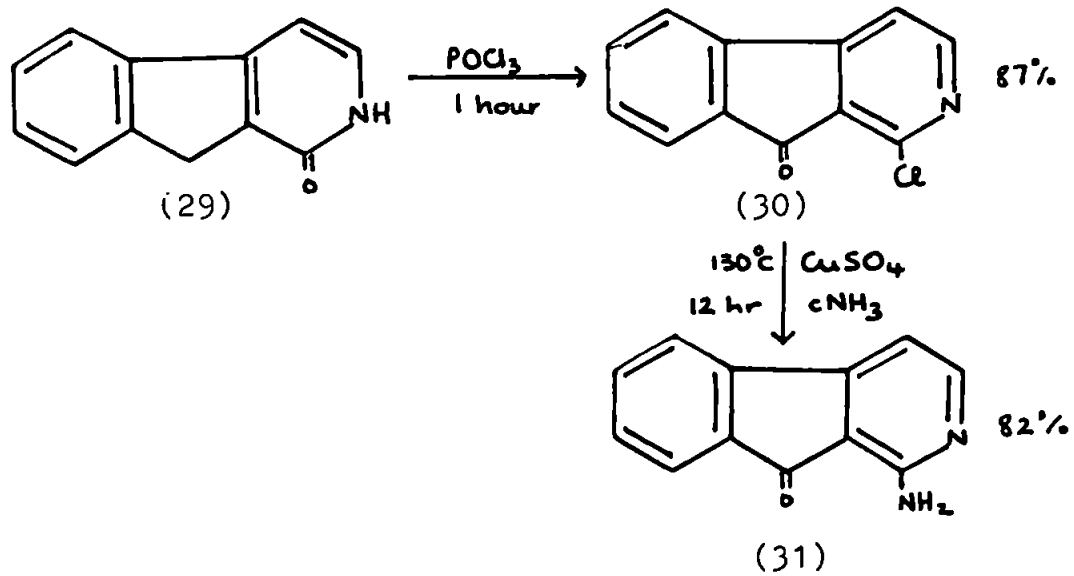
When heated with ammonia, under pressure, (27) afforded the natural compound indeno[1,2,3-ij][2,7]naphthyridine or trivial name - eupolauridine (28) as the main product. Scheme 13.



(26) (27) (28)

Scheme 13

Treatment of (29), by Bowden[22], with phosphorus oxychloride yielded 1-chloro-9H-indeno[2,1-c]pyridin-9-one (30) which was converted by ammonia, in the presence of a copper sulphate catalyst , into the amine (31). Scheme 14.



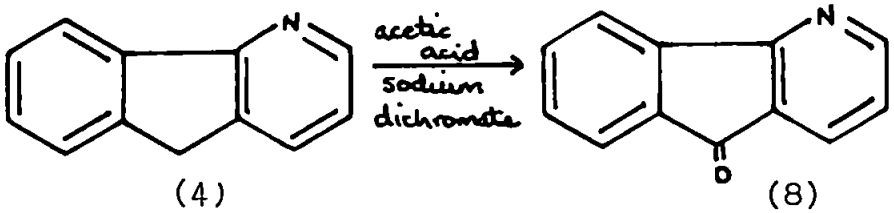
(29) (30) (31)

Scheme 14

c. Reactivity of the Methylene Group.

1. Oxidation.

Riverschi[23] oxidised 5H-indeno[1,2-b]pyridine (4) by reaction in acetic acid with sodium dichromate, to afford 5H-indeno[1,2-b]pyridin-5-one (8) in 81% yield. Scheme 15.

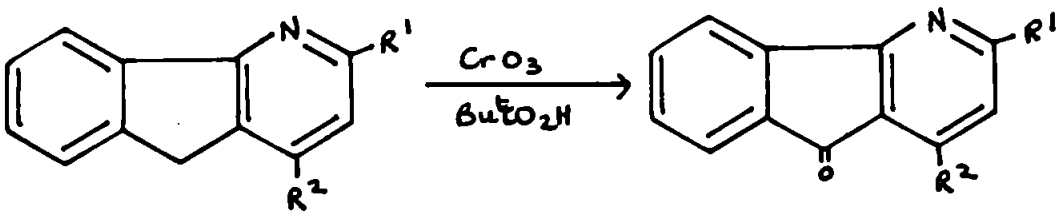


(4) (8)

Scheme 15

DuPriest et al[24] obtained the oxo compound (8) in 36% yield by bubbling oxygen into a pyridine solution of 5H-indeno-[1,2-b]pyridine and Triton B.

Nitta et al[25] effected oxidation by refluxing a solution of 2-methyl-5H-indeno[1,2-b]pyridine (32), chromium trioxide and a seven fold excess of butyric acid in DCM. 2-Methyl-5H-indeno[1,2-b]pyridin-5-one (33) was obtained in 62% yield. Nitta et al[25] also oxidised other indenopyridine derivatives in good yield, as shown in Scheme 16.



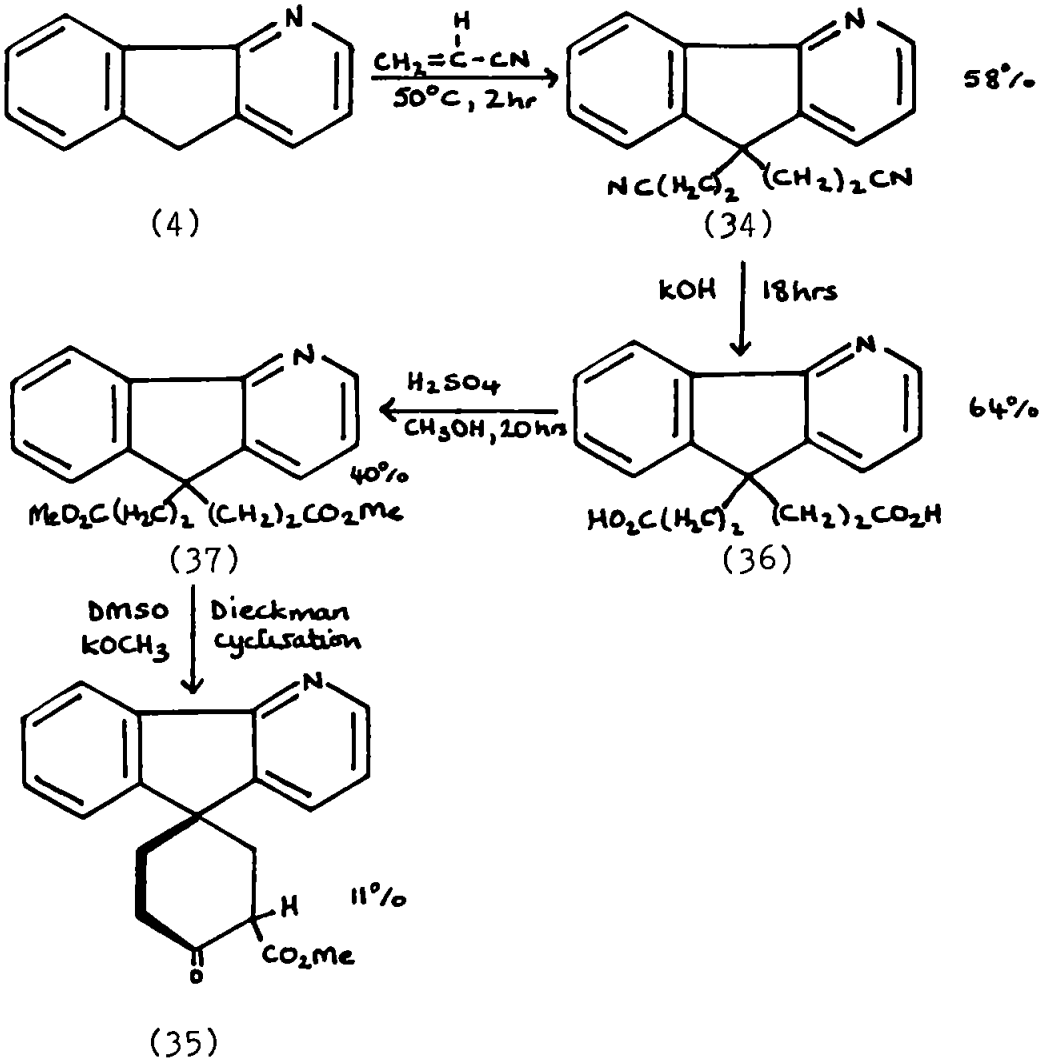
R'=Me ; R^2=H (32)	R'=Me ; R^2=H (33) (62%)
R'=Ph ; R^2=H	R'=Ph ; R^2=H (89%)
R'=R^2=Ph	R'=R^2=Ph (88%)
R'=Me ; R^2=Ph	R'=Me ; R^2=Ph (73%)
R'=H ; R^2=Me	R'=H ; R^2=Me (33%)

Scheme 16

2. Substitution reactions

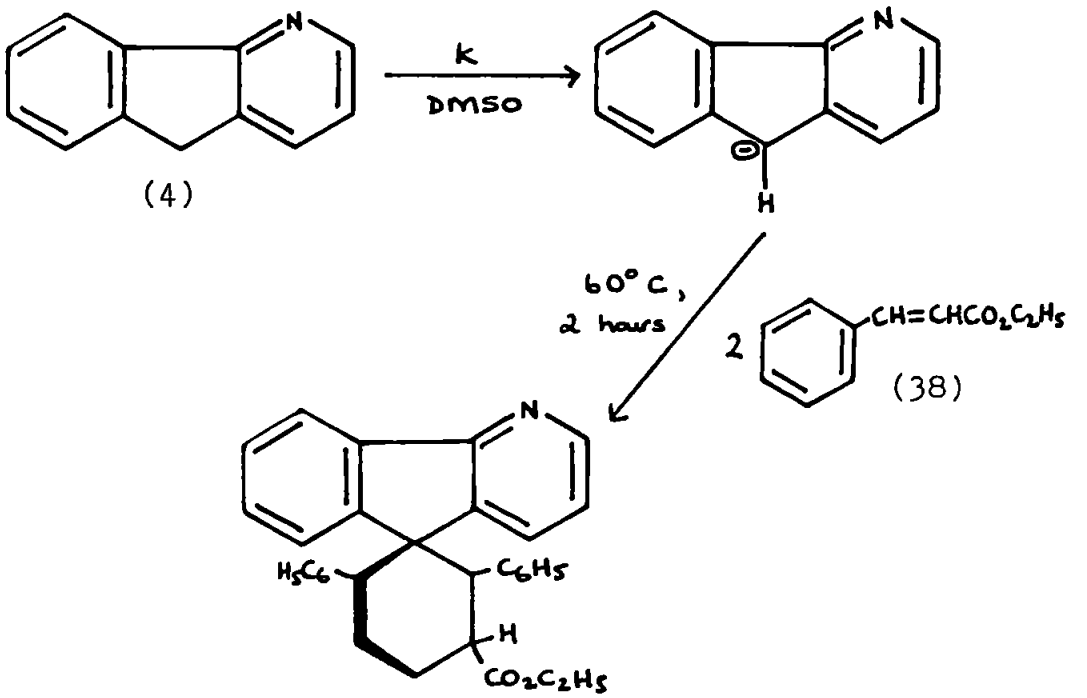
Substitution reactions of the methylene protons of the indenopyridines have been investigated by Prostakov et al[26,27]. All of the reactions reported involved nucleophilic attack by the indenopyridine carbanion on an electrophile. One such reaction involved the preparation of cyanoethyl derivatives of indenopyridines (4) and (1).

For example, 5,5'-bis-cyanoethylindeno[1,2-b]pyridine (34) was obtained by cyanoethylation of 5H-indeno[1,2-b]pyridine (4). Compound (34) was then converted to methyl 5H-indeno-[1,2-b]pyridin-5-spiro-1(cyclohexane-4'-oxo-3'-carboxylate) (35) via the diacid (36) and diester (37). Scheme 17.



Scheme 17

A more direct route to spiro compounds involved reaction of of the carbanion, obtained by treatment of (4) with potassium in dimethylsulphoxide, with ethyl cinnamate (38) to afford ethyl 5H-indeno[1,2-b]pyridin-5-spiro-1(cyclohexane-2',6'-diphenyl-3'-carboxylate),(39), as shown in Scheme 18.



(4)

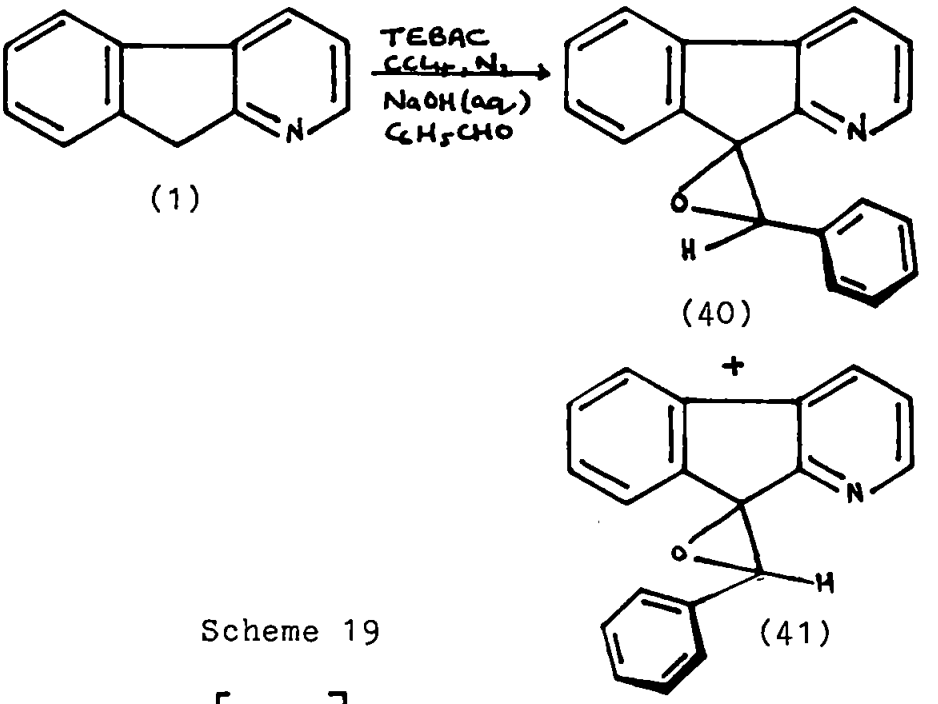
(38)

(39)

Scheme 18

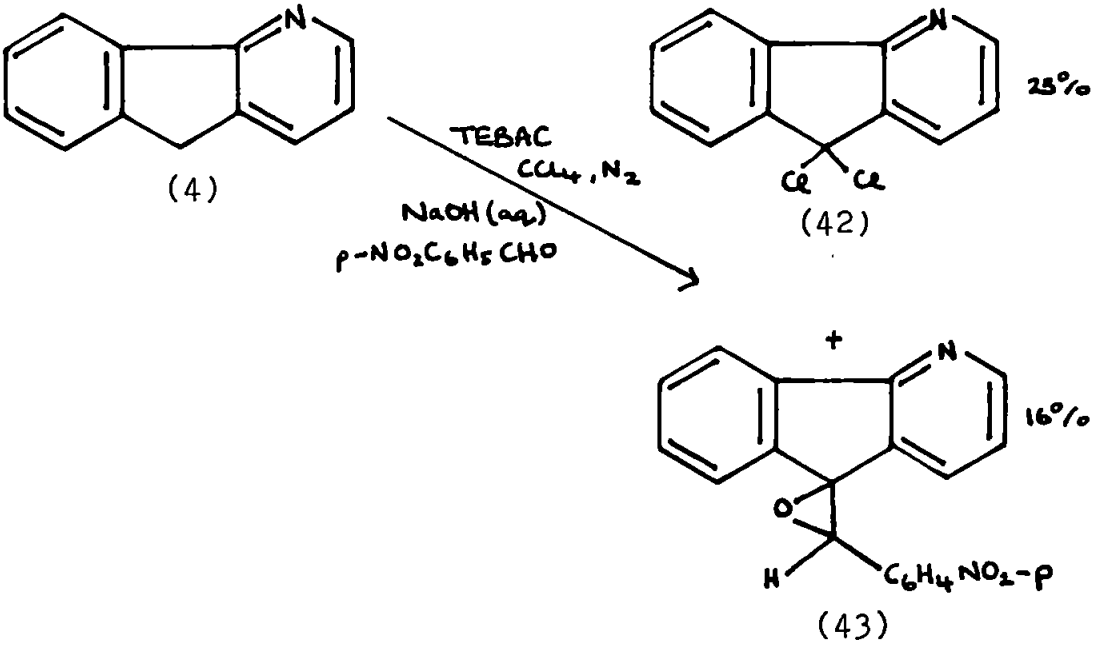
Prostakov and coworkers [26] obtained spiro compounds of indenopyridines in up to 50% yields using Darzens method under phase-transfer catalysis conditions.

For example, 9H-indeno[2,1-b]pyridine (1), on condensation with benzaldehyde in the presence of 50% aqueous sodium hydroxide solution, carbon tetrachloride and catalytic amounts of triethylbenzylammonium chloride (TEBAC), gave the spiro compounds (40, 41) in a combined yield of 24%. Scheme 19.



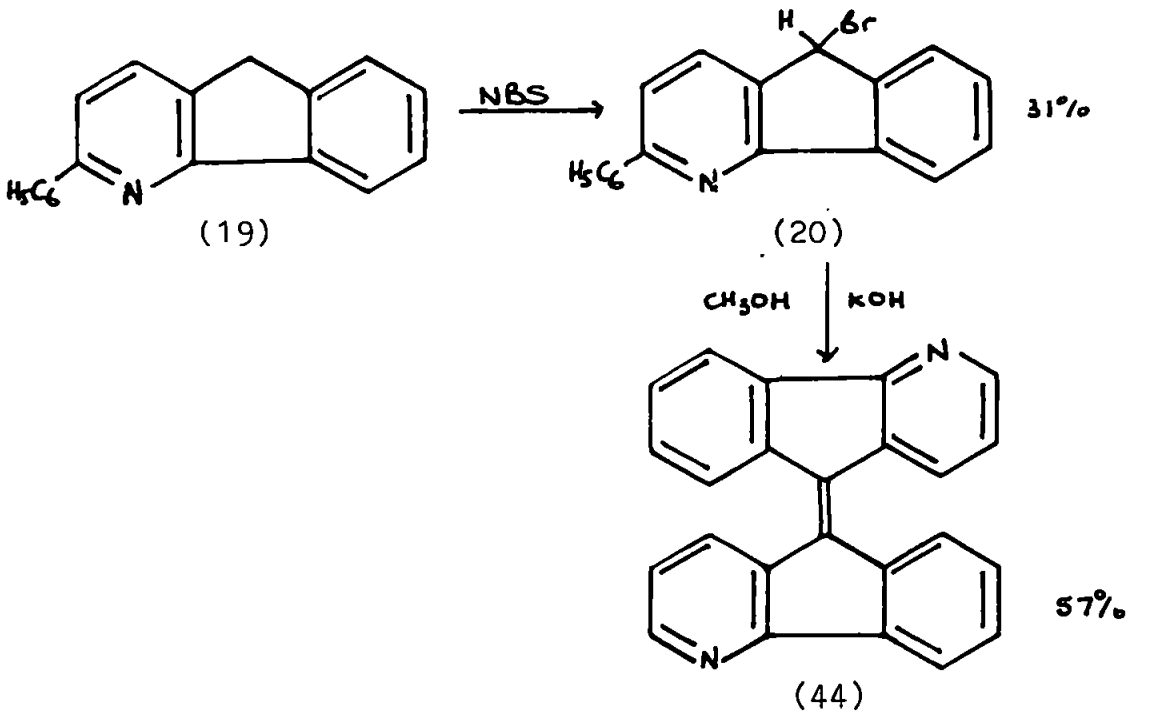
Scheme 19

When 5H-indeno[1,2-b]pyridine (4) was treated with p-nitrobenzaldehyde under phase-transfer catalysis conditions[26], the principal products were the dichloro-compound (42) and the spiro compound (43).Scheme 20.



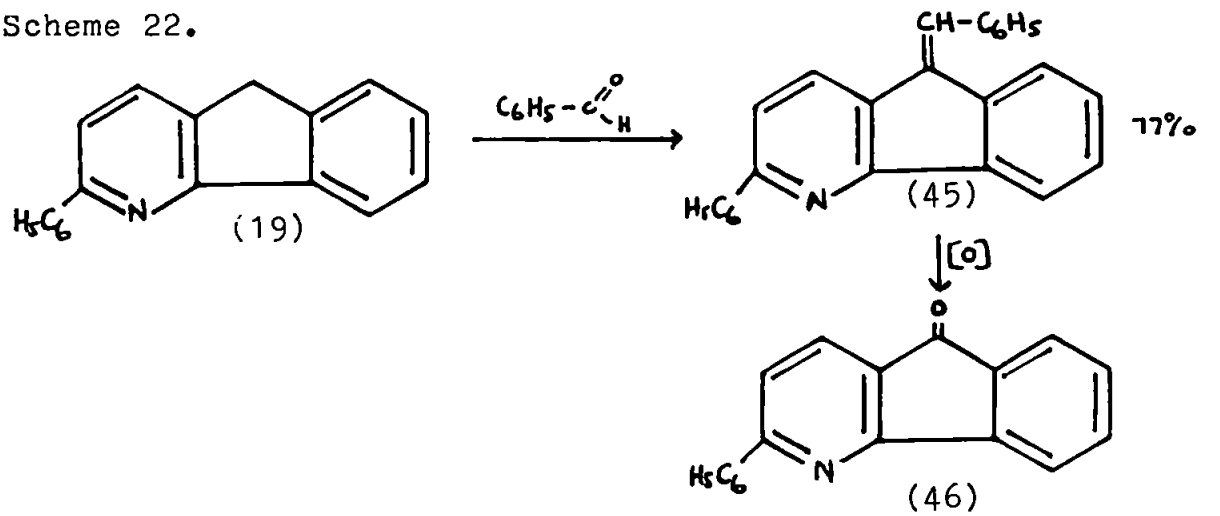
Scheme 20

Pavel et al[16] have prepared several derivatives of (4) For example, reaction of 2-phenyl-5H-indeno[1,2-b]pyridine (19) with NBS afforded (20) in 31% yield. Reaction of (20) with potassium hydroxide in methanol afforded the dimer (44). Scheme 21.



Scheme 21

When (19) was reacted with benzaldehyde in acetic anhydride/ acetic acid, the 5-benzylidene derivative (45) was obtained in 77% yield. Oxidation gave the corresponding ketone (46). Scheme 22.

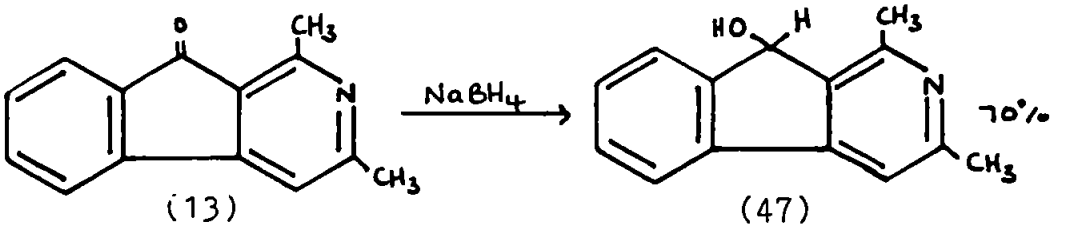


Scheme 22

d. Addition to the Carbonyl group of Indenopyridones.

i. Reduction to alcohols.

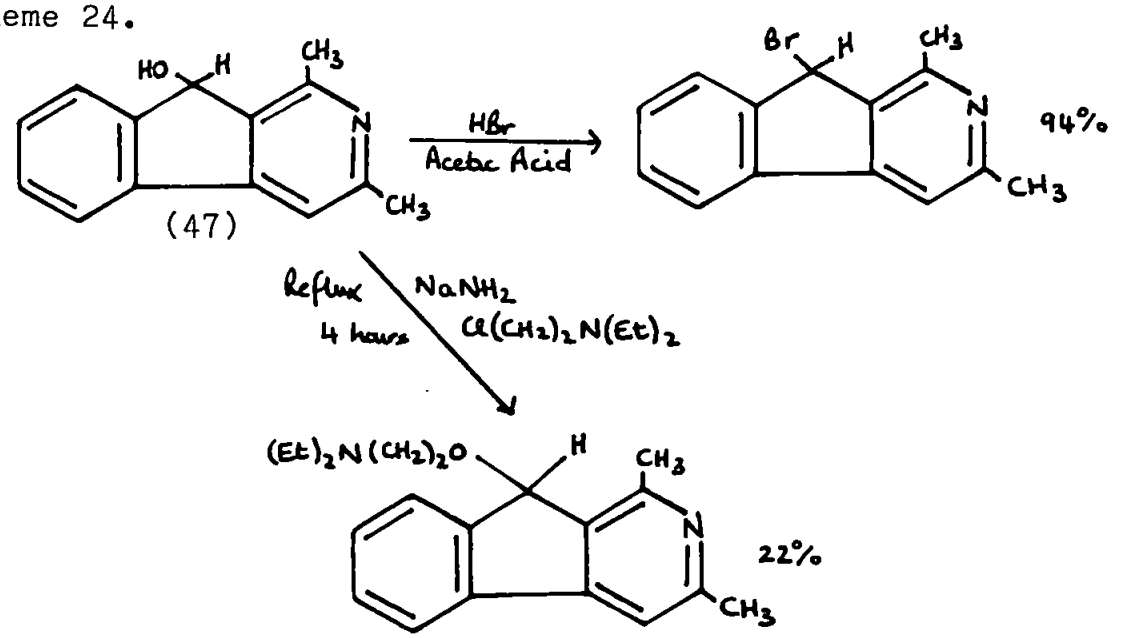
The oxo derivatives of indenopyridines undergo typical reactions of the carbonyl group. The ketones are easily reduced with sodium borohydride or zinc in aqueous acid to give the hydroxy compound [14] .For example, reduction of 1,3-dimethyl-9H-indeno[2,1-c]pyridin-9-one (13) gave 1,3-dimethyl-9-hydroxy-9H-indeno[2,1-c]pyridine(47) in 70% yield.Scheme 23.



(13) (47)

Scheme 23

Feitelson and Petrow [28] used the above alcohol (47) as starting material for further synthesis, as shown in Scheme 24.

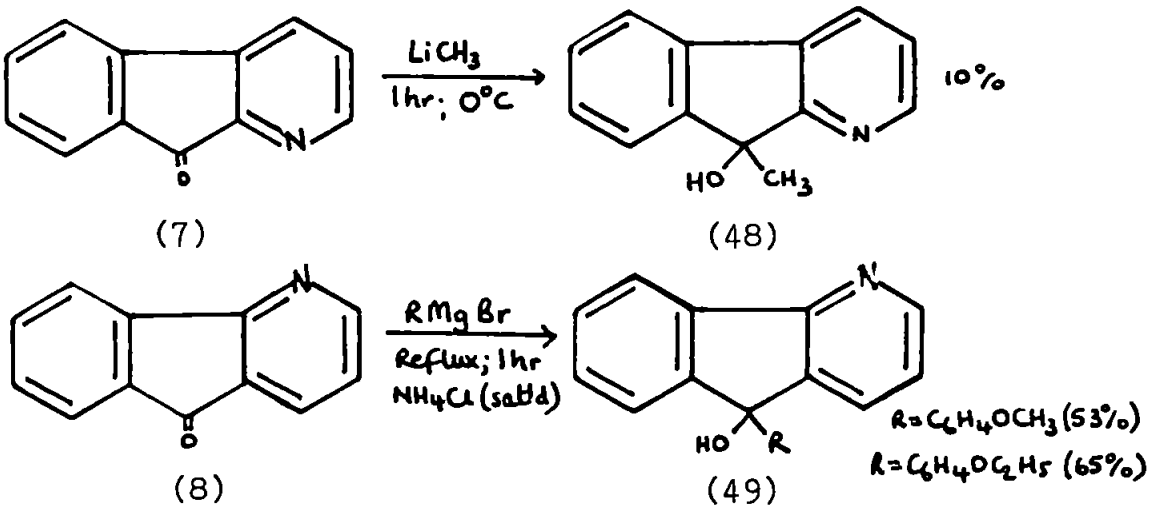


(47)

Scheme 24

ii. Reaction with Grignard reagents and Organometallic compounds.

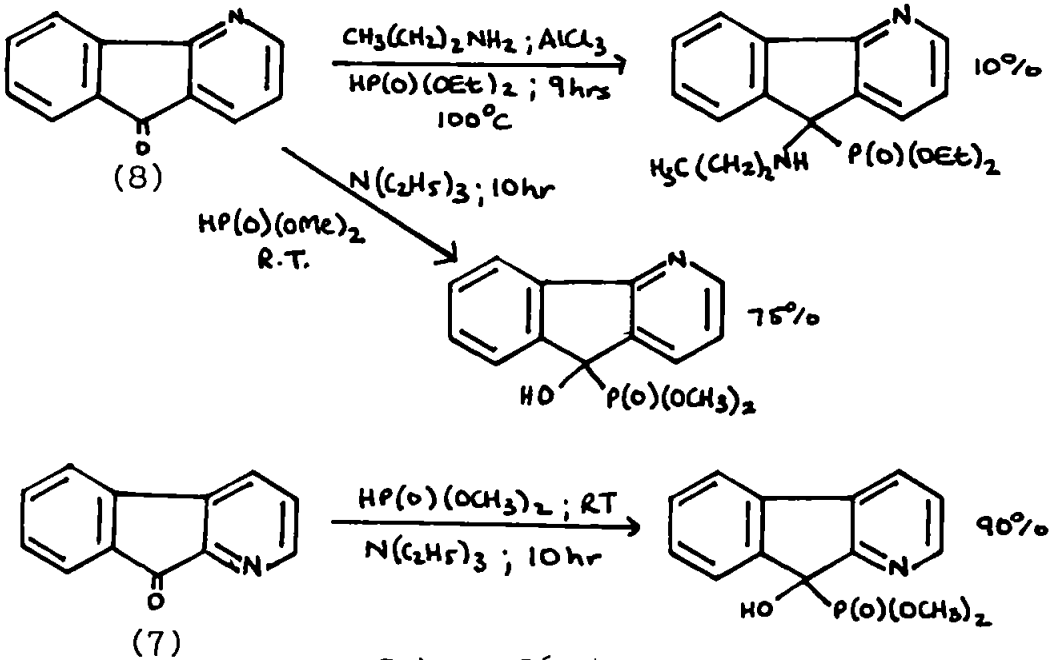
The carbonyl compounds also react with Grignard reagents and organometallic compounds such as lithium alkyls. Prostakov [29] has reported the preparation of α-hydroxyaryl and alkyl derivatives (48,49) of (7) and (8).Scheme 25.



Scheme 25

iii. Reaction with phosphonic acid.

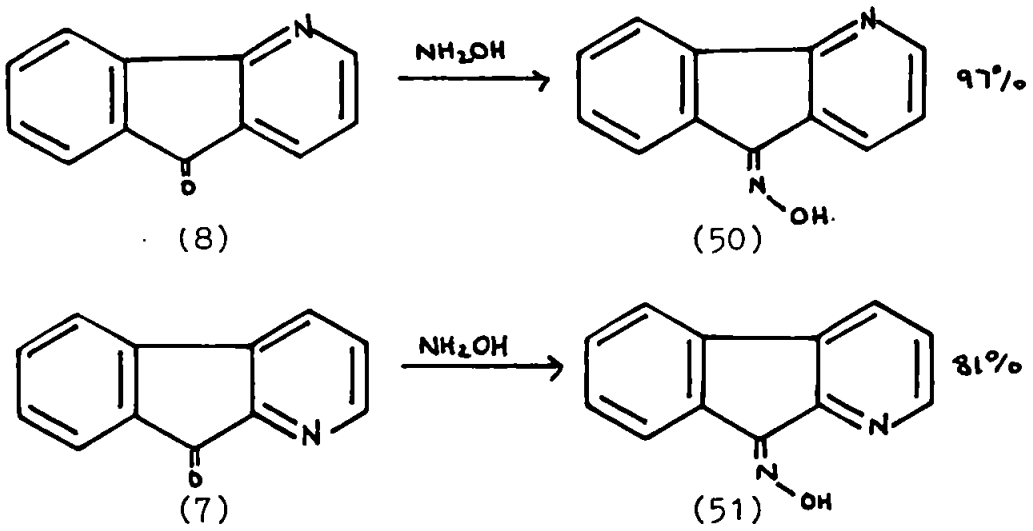
Wieczorok et al [30] have prepared several phosphonic acid derivatives of the indenopyridines as analogues of morphactins.The synthetic route is shown in Scheme 26.



Scheme 26

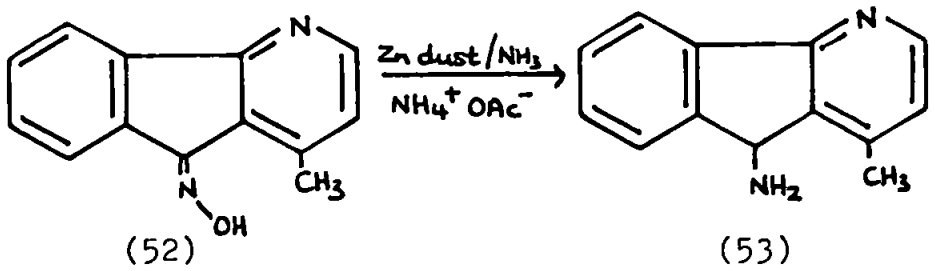
iv. Oxime formation

Another standard reaction of carbonyl groups is the formation of oximes. Kloc et al[31] obtained 5H-indeno-[1,2-b] pyridin-5-one oxime (50) and 9H-indeno[2,1-b]-pyridin-9-one oxime (51) in excellent yields by reaction of the ketones (8 and 7) with hydroxylamine.Scheme 27.



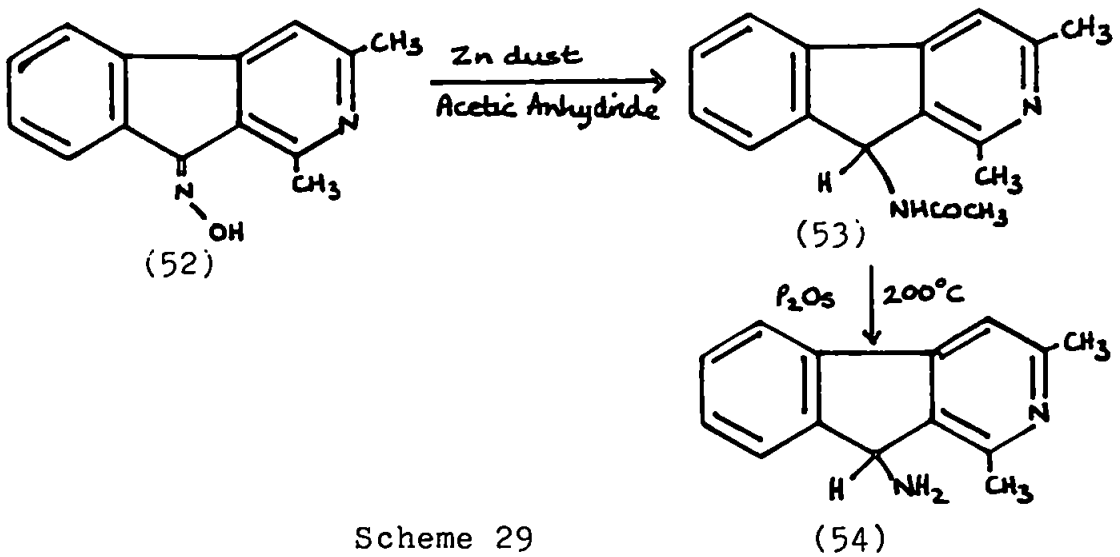
Scheme 27

Bowden and coworkers [22] used 4-methyl-5H-indeno[1,2-b]-pyridin-5-one oxime (52) to obtain the amine (53) by reduction using zinc dust/ammonia and ammonium acetate. Scheme 28.



Scheme 28

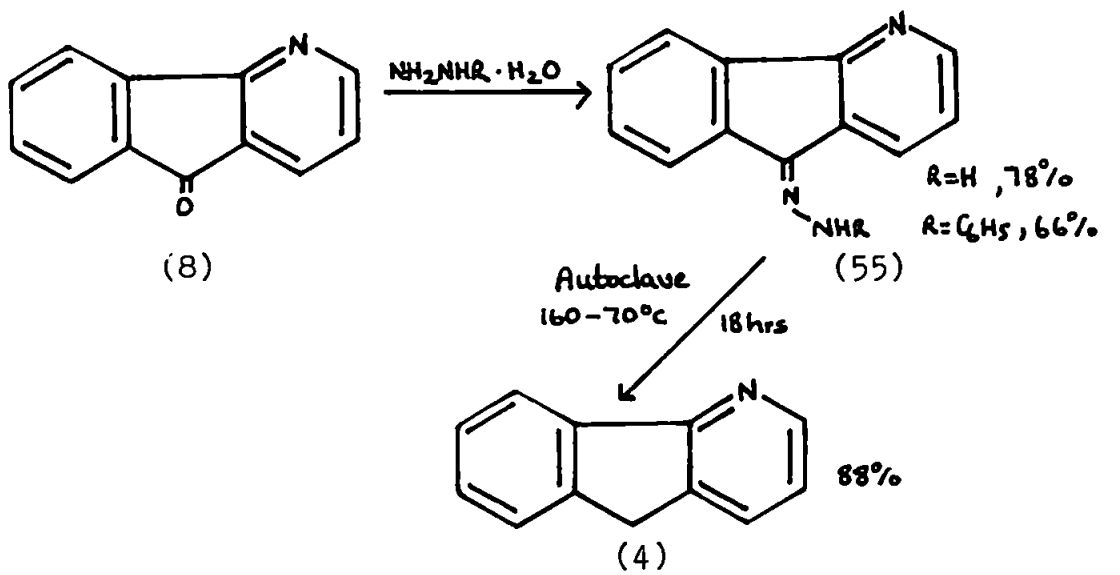
Petrow et al [12] starting from 1,3-dimethyl-9H-indeno[2,1-c]-pyridin-9-one oxime (52) , obtained the 9-acetamido derivative (53), which on treatment with phosphoric acid at 200°C , afforded the 9-amino compound (54) in 94% yield. Scheme 29.



Scheme 29

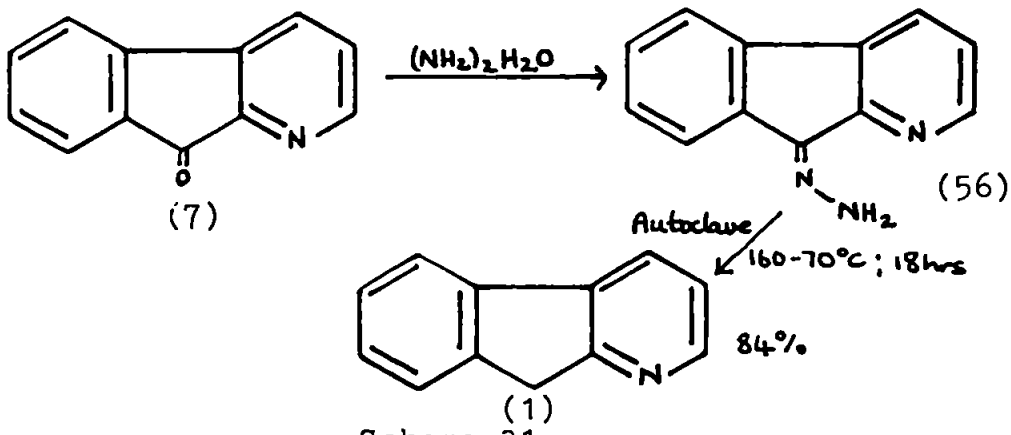
v. Reduction of the Carbonyl group.

Reduction can be achieved using Wolff-Kishner conditions as described by Mlochowski et al [32] . Through the intermediate hydrazone (55), 5H-indeno[1,2-b]pyridine (4) was obtained in 88% yield .Scheme 30.



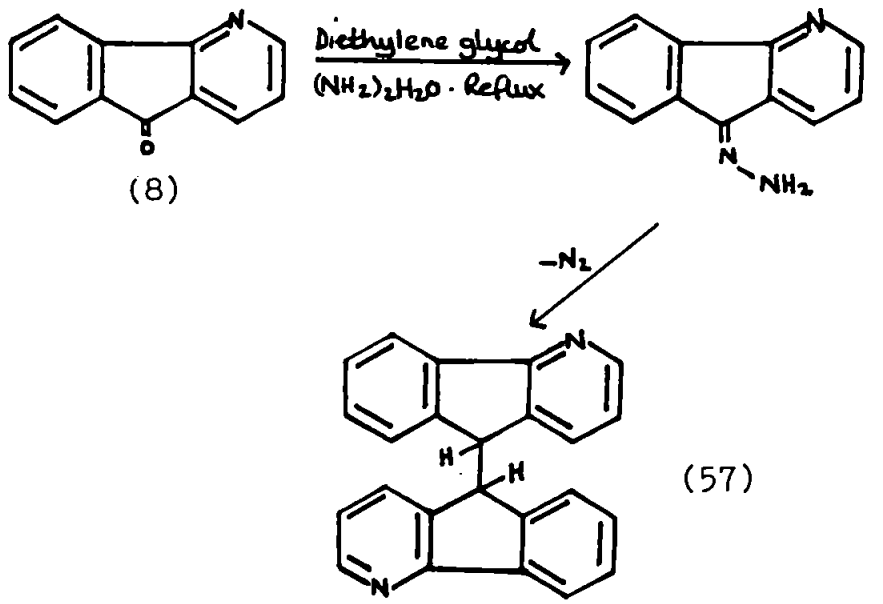
Scheme 30

Likewise, 9H-indeno[2,1-b]pyridine (1) was obtained from the intermediate hydrazone (56) in 84% yield.Scheme 31.



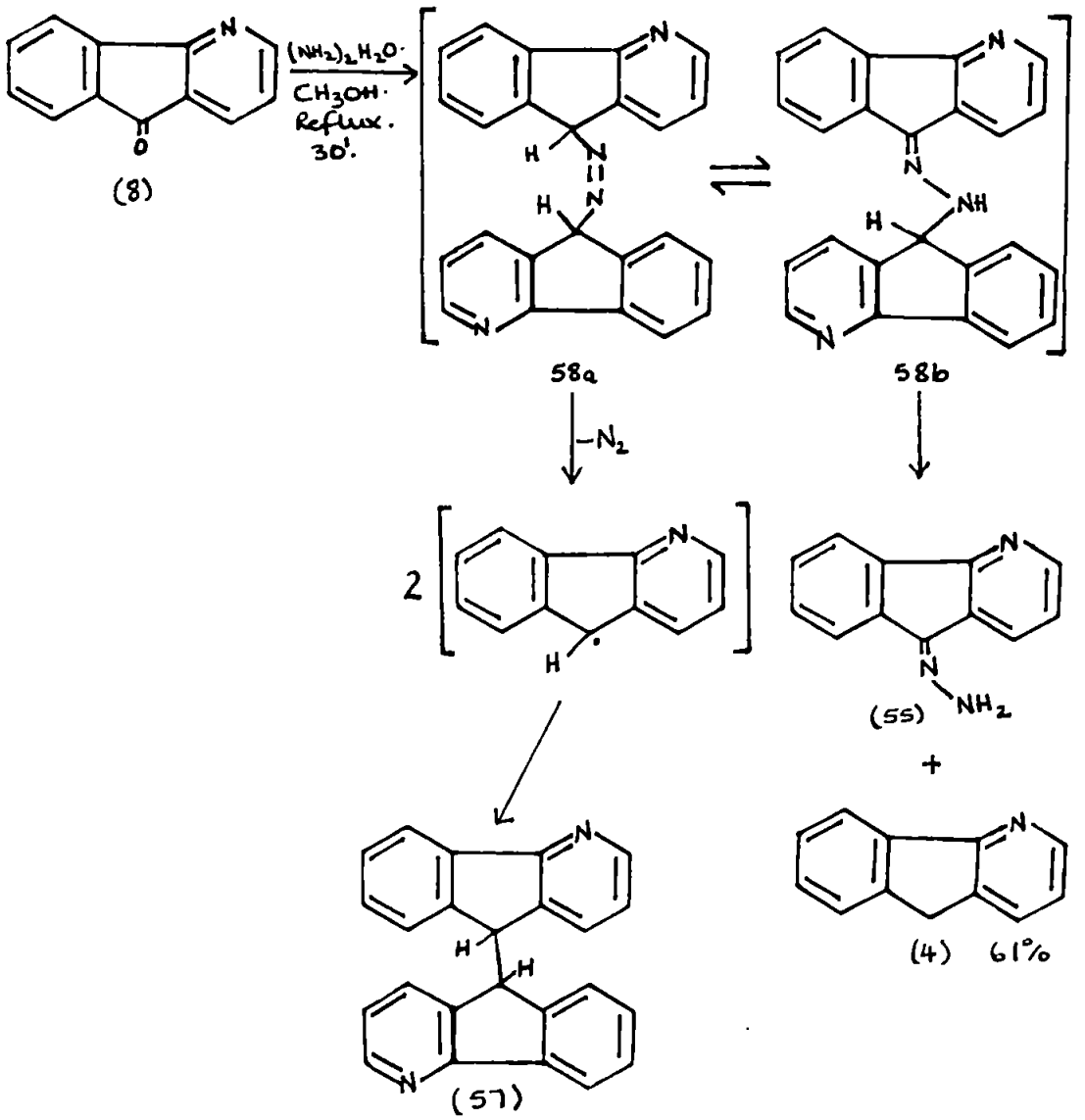
Scheme 31

When using the Huang-Minlon modification for the reduction of (4), these workers[32] also observed the formation of a dimeric compound in 11% yield. Even when using an excess of hydrazine, the dimer (57) was still formed. Scheme 32.



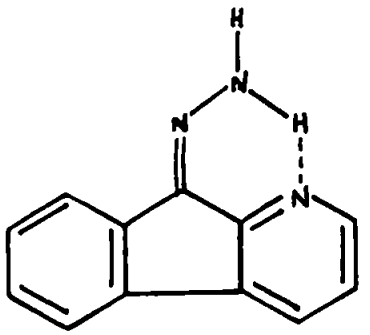
Scheme 32

It has been suggested by Eda et al[33] and Mlochowski and Szulc[34] that the dimer (57) arises from the recombination of radicals formed as a result of elimination of nitrogen from the intermediate (58), as shown in Scheme 33.



Scheme 33

Reduction of 9H-indeno[2,1-b]pyridine-9-one (7) gave only the reduced compound (1) and none of the corresponding dimeric compound. With this isomer, the hydrazone (56) is stabilized by formation of an intramolecular hydrogen bond which prevents formation of the analogue intermediate (58a).Scheme 33.

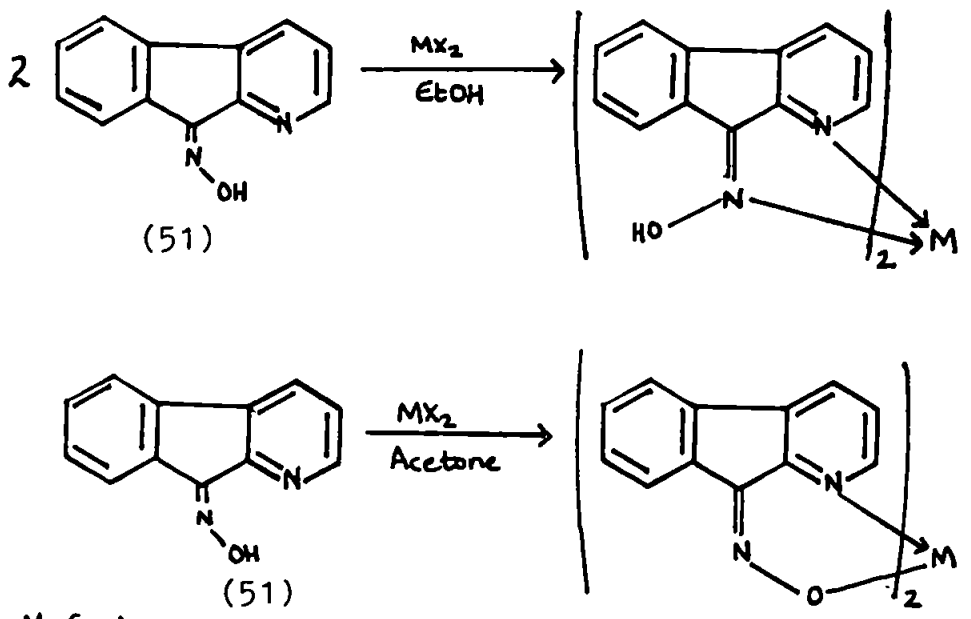


(56)

e. Miscellaneous reactions of Indenopyridines.

1. Formation of co-ordination compounds.

Zaitzev [35] reported that the oxime of 9H-indeno[2,1-b]-pyridine (51) can form chelate complexes with silver or copper.Neutral or charged complexes are formed, depending on the preparative method used.Scheme 34.

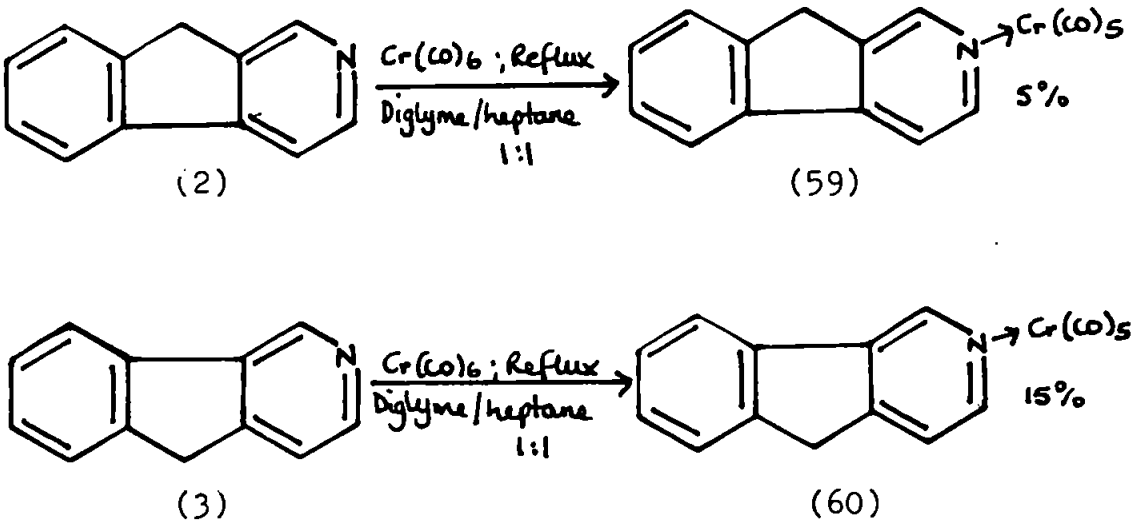


Scheme 34

2. Formation of tricarbonylchromium complexes.

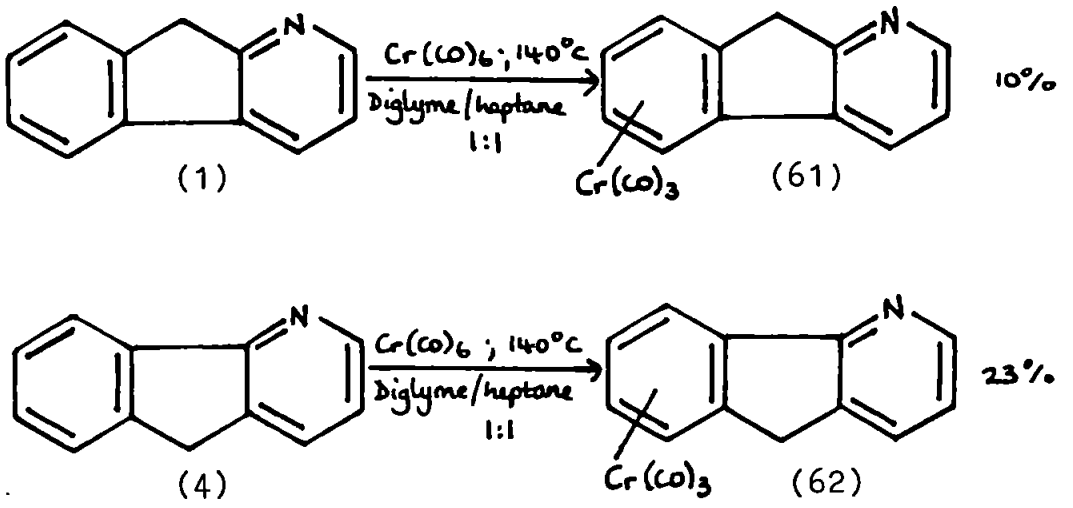
Nesmeyanov and Ustynyuk [36] have synthesised several N-donor and n^6 complexes using indenopyridines (1,2,3 & 4) and transition metal carbonyls.

In all cases (2) and (3) formed only N-donor complexes of the $LCr(CO)_5$ type; compounds 59 and 60. Scheme 35.



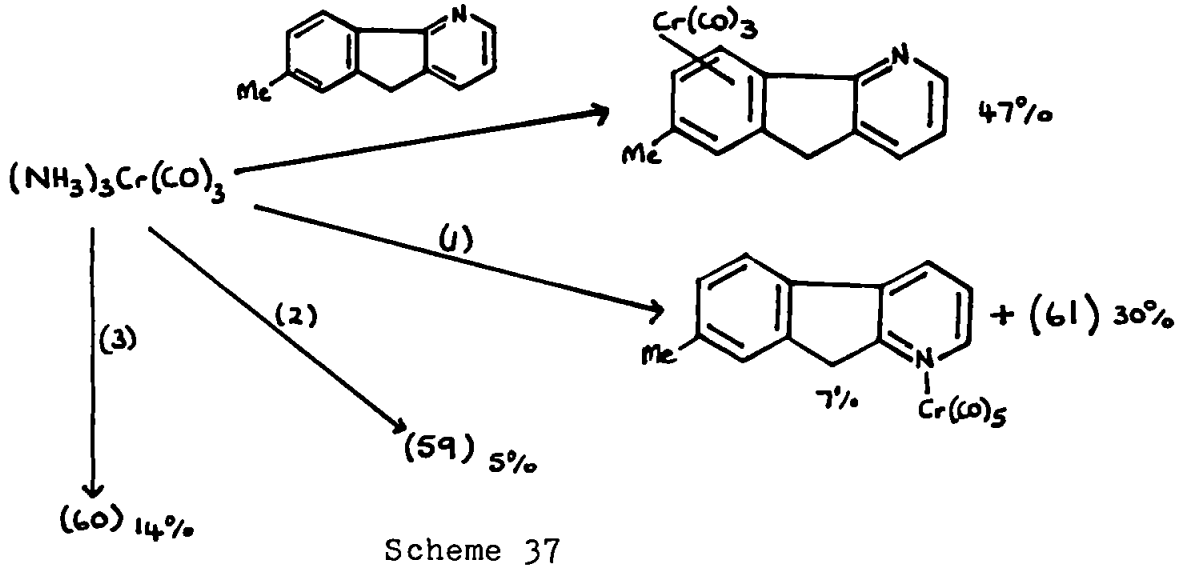
Scheme 35

In the case of the other indenopyridines (1 and 4), co-ordination occurs at the benzene ,rather than the heterocyclic, ring, giving compounds 61 and 62.Scheme 36.



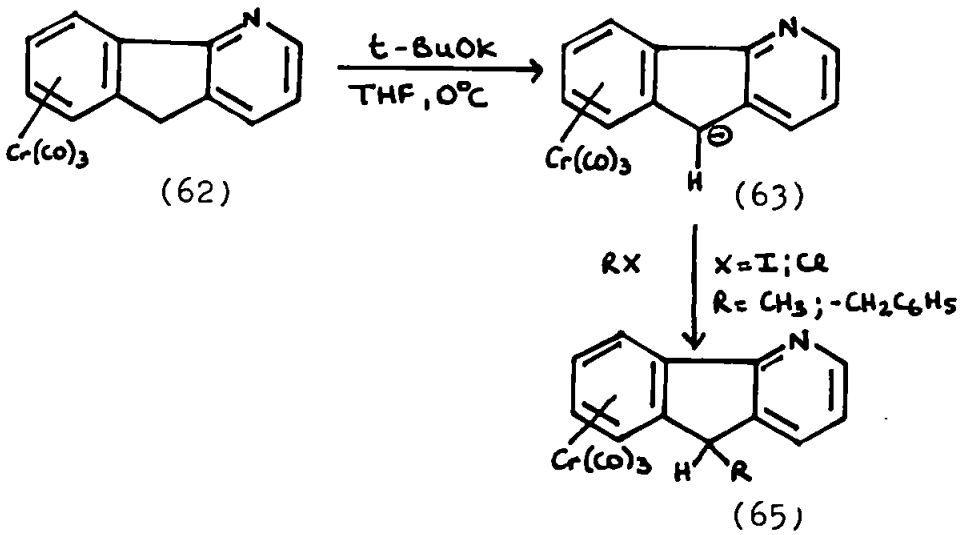
Scheme 36

When indenopyridines were treated with trisamino-chromiumtricarbonyl [36] in boiling dioxan , mixtures of the n^6 -arene and N-donor complexes were formed.Scheme 37.



Scheme 37

The reactivity of these n^6 -complexes was studied; it was found that the complex could be deprotonated at the methylene bridge enabling the resultant carbanions (63 and 64) to be alkylated (65) and acylated (66).Scheme 38.



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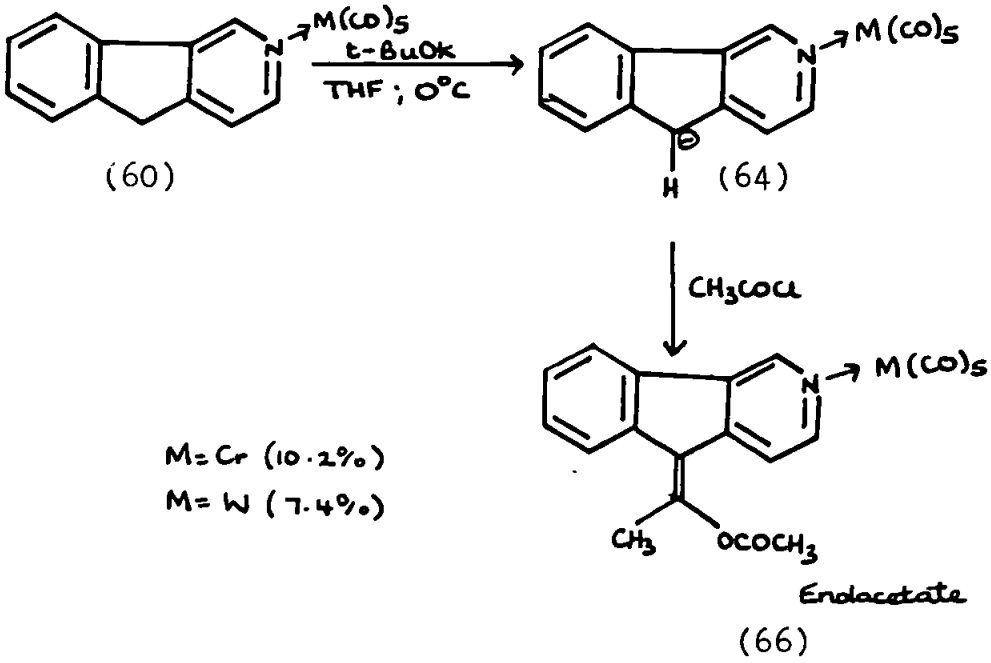


(60) (64) (66)

M = Cr (10.2%)
M = W (7.4%)

Scheme 38

Chapter 4. Early Indenopyridine Synthesis.

The synthesis of indenopyridines may be divided into three types.

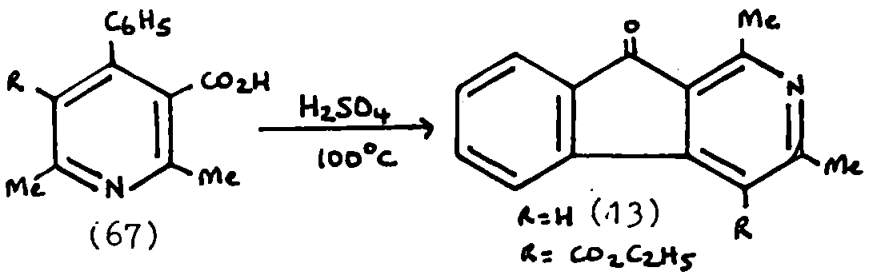
Type 1. Syntheses resulting from the formation of the cyclopentane ring by cyclisation of a substituted phenyl pyridine.

Type 2. Syntheses involving construction of the pyridyl ring using indene as starting material.

Type 3. Syntheses involving ring contraction of benzoquinoline.

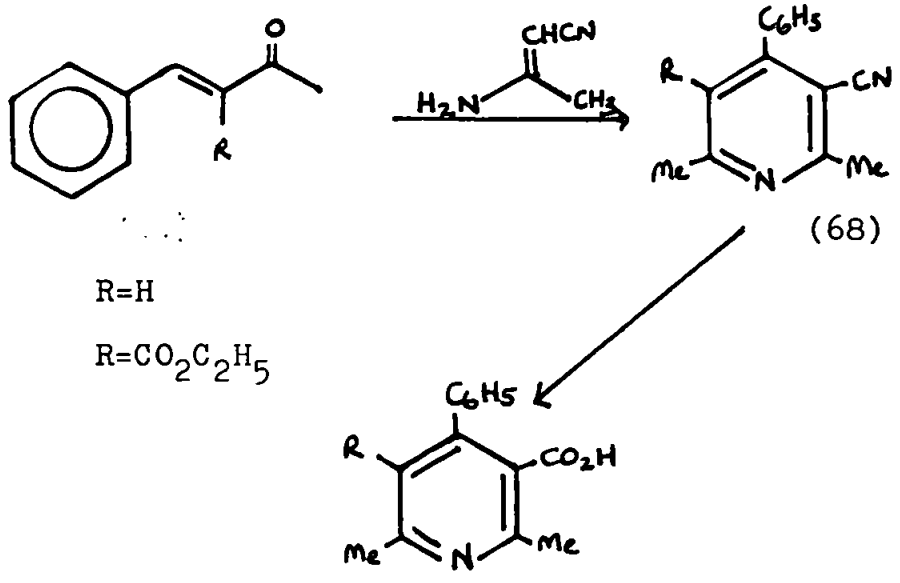
Type 1. Syntheses involving Formation of a Cyclopentane ring.

Subsequent to the report already cited[3], synthetic routes to this ring system received very little attention until 1924 when Mills et al[37] synthesized 1,3-dimethyl-9H-indeno[2,1-c]pyridin-9-one (13) in 90% yield by cyclisation of 2,6-dimethyl-4-phenylpyridine carboxylic acid (67,R=H) and the ethyl carboxylate derivative by cyclisation of ethyl 3-carboxy-2,6-dimethyl-4-phenylpyridine-5-carboxylate (67, R=$CO_2C_2H_5$). Scheme 39



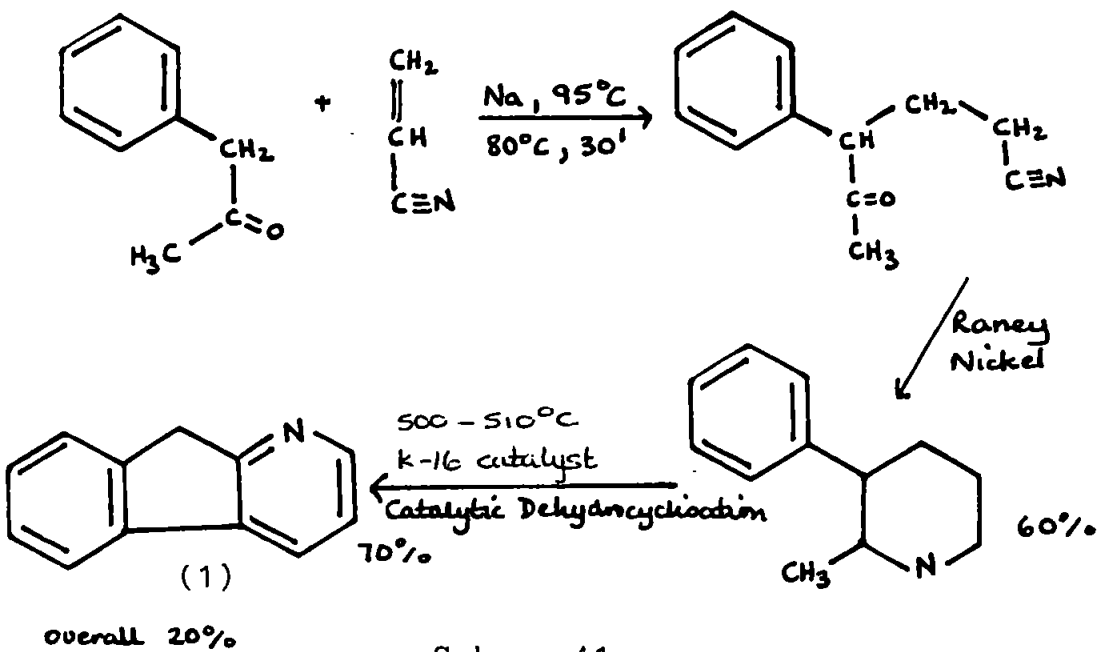
Scheme 39

The starting material used for cyclisation was prepared by hydrolysis of the 3-carbonitrile group of 2,6-dimethyl-4-phenylpyridine-3-carbonitrile (68,R=H),or ethyl 3-cyano-2,6-dimethyl-4-phenylpyridine-5-carboxylate (68,R=$CO_2C_2H_5$).Scheme 40.



Scheme 40

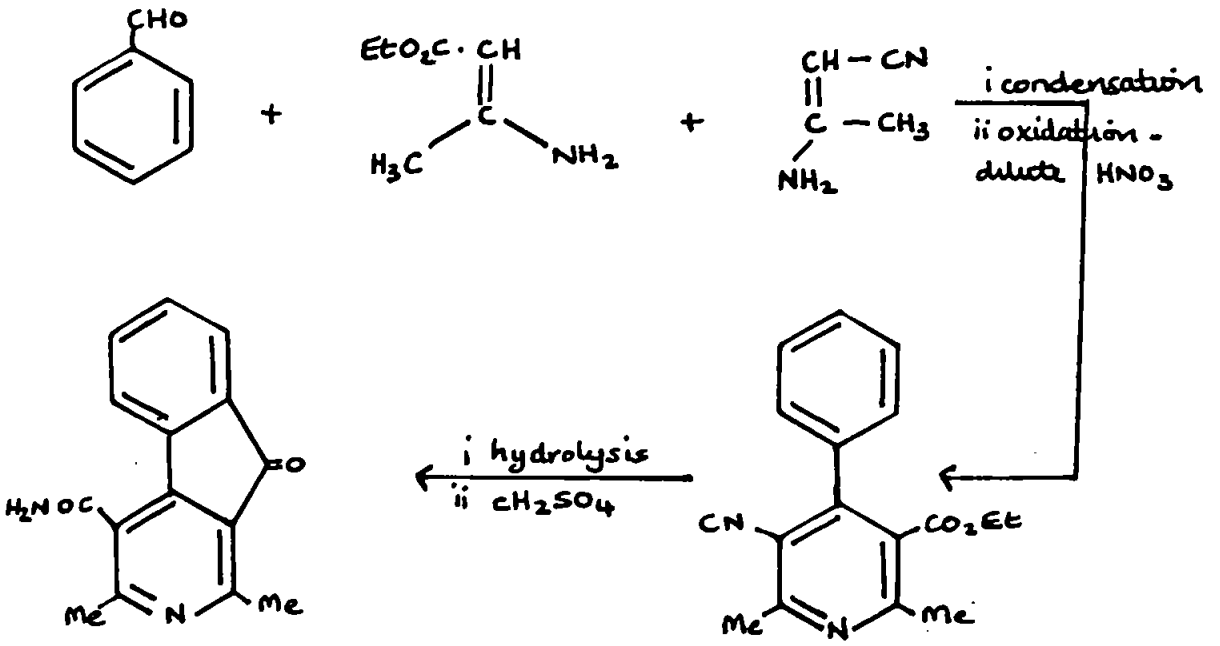
The same approach was used by Urbina [38] for the preparation of 9H-indeno[2,1-b]pyridine (1). Scheme 41.



Scheme 41

A similar approach was used by Petrow [12] in 1946. Condensation of benzaldehyde with β-aminocrotonitrile and ethyl-β-aminocrotonitrile led to the formation of

ethyl 5-cyano-2,6-dimethyl-4-phenyldihydropyridine-3-carboxylate which is easily oxidised by dilute nitric acid to ethyl 5-cyano-2,6-dimethyl-4-phenylpyridine-3-carboxylate (68,R=$CO_2C_2H_5$).Hydrolysis furnished the corresponding acid which was converted to 1,3-dimethyl-9-oxo-9H-indeno[2,1-c] pyridine-4-carboxamide (69). Scheme 42.

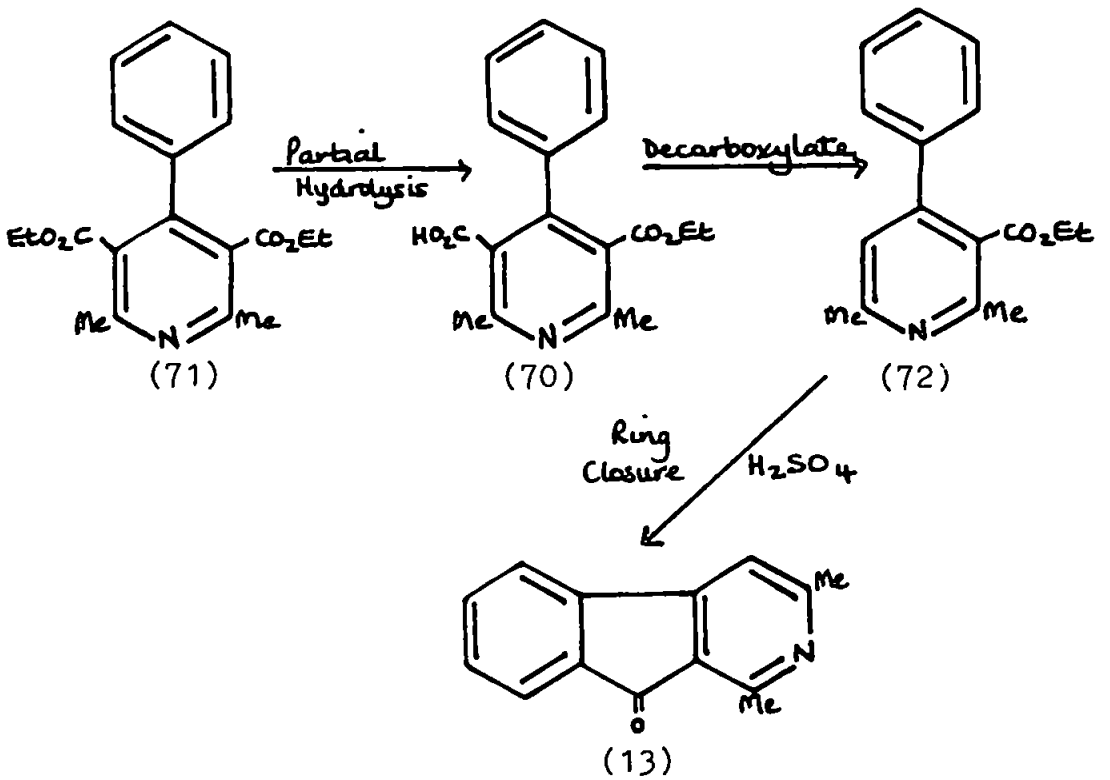


(69) (68)

Scheme 42

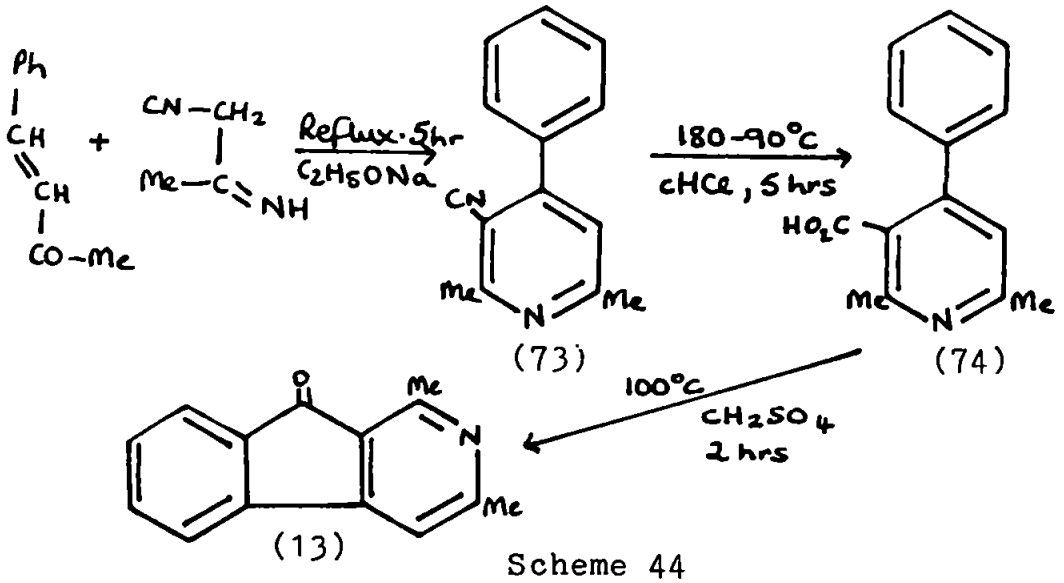
Similarly,in 1949,Petrow and Kahn[14] synthesized 1,3-dimethyl-9H-indeno[2,1-c]pyridin-9-one (13) essentially as described by Mills et al[37] but the intermediate acid ester (70) was decarboxylated by heating in a neutral solvent such as liquid paraffin. Diethyl 2,6-dimethyl-4-phenylpyridine-3,5-carboxylate (71) was converted into the acid ester (70) by partial hydrolysis. Decarboxylation afforded ethyl 2,6-dimethyl-4-phenylpyridine-3-carboxylate (72).Hydrolysis followed by treatment with sulphuric acid(dilute), gave 2,6-dimethyl-4-phenylpyridine-3-carboxylic acid sulphate

which gave (13) in 90% yield by ring closure with sulphuric acid.Scheme 43.



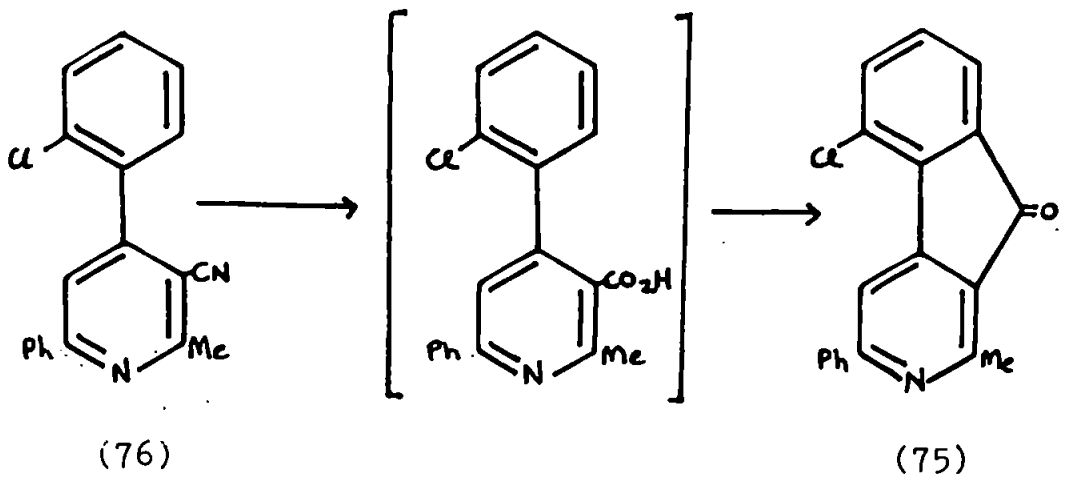
Scheme 43

Following Petrow's work, Chatterjea[39] in 1952 synthesized (13) from 3-cyano-2,6-dimethyl-4-phenylpyridine. Acetodinitrile (β -aminocrotonitrile) was reacted with benzal-acetone, albeit in poor yield, to give 3-cyano-4-phenyl-lutidine (73).The cyanopyridine (73) on hydrolysis with hydrochloric acid at 180-190°C furnished 2,6-dimethyl-4-phenylpyridine-3-carboxylic acid (74), which on treatment with concentrated sulphuric acid at 100°,cyclised to (13). Scheme 44.



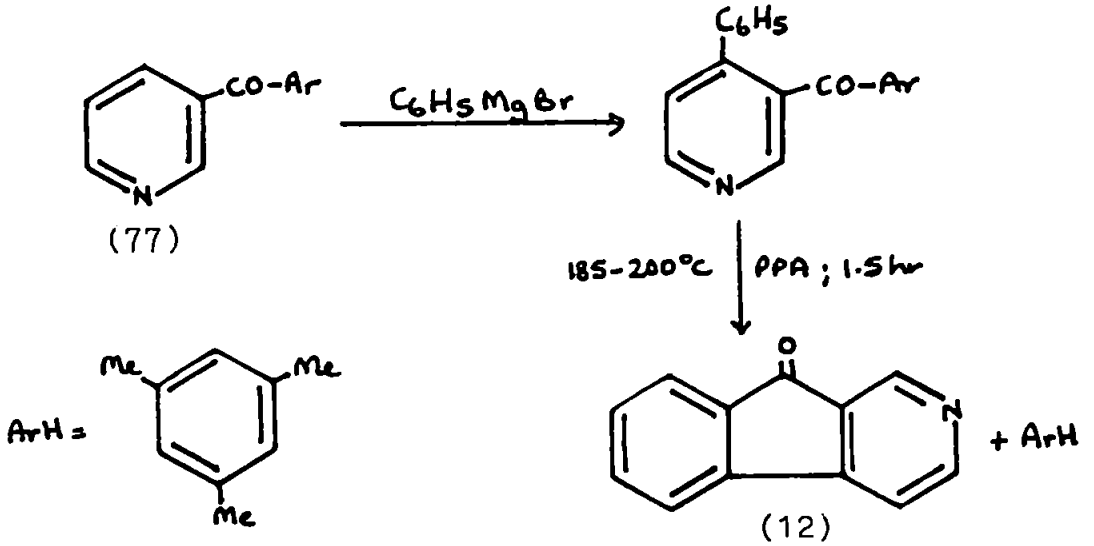
Scheme 44

Chatterjea and Prasad[40], extended this synthesis to the chloro- derivative of 1-methyl-3-phenyl-9H-indeno[2,1-c]-pyridin-9-one (75). Reaction of o-chlorobenzylidene-acetophenone and aminoacrylonitrile gave the aryl pyridine (76), Oxidation with dilute nitric acid or chromic acid in acetic acid gave the corresponding cyanopyridine which was converted to 5-chloro-1-methyl-3-phenyl-9H-indeno[2,1-c]-pyridin-9-one (75) by heating with concentrated sulphuric acid at 100°C for 0.5 hours. Scheme 45.



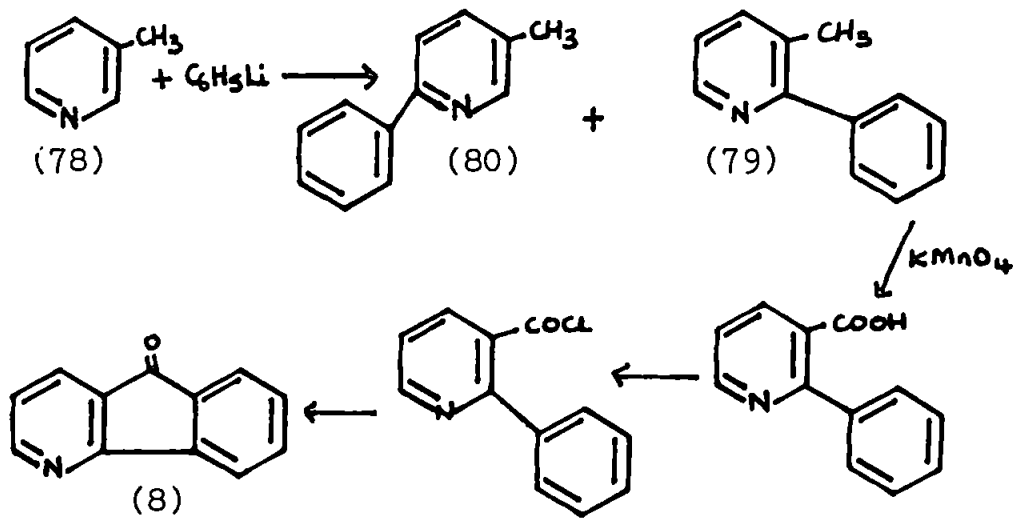
Scheme 45

Fuson and Miller[41] and Périn-Roussel and Jacquingnon[13] prepared 9H-indeno[2,1-c]pyridin-9-one (12) in 19% and 23% yields respectively. Because the ketone (77) is hindered the Grignard reagent does not attack the carbonyl group, instead (77) is phenylated in the 4 position. Scheme 46.



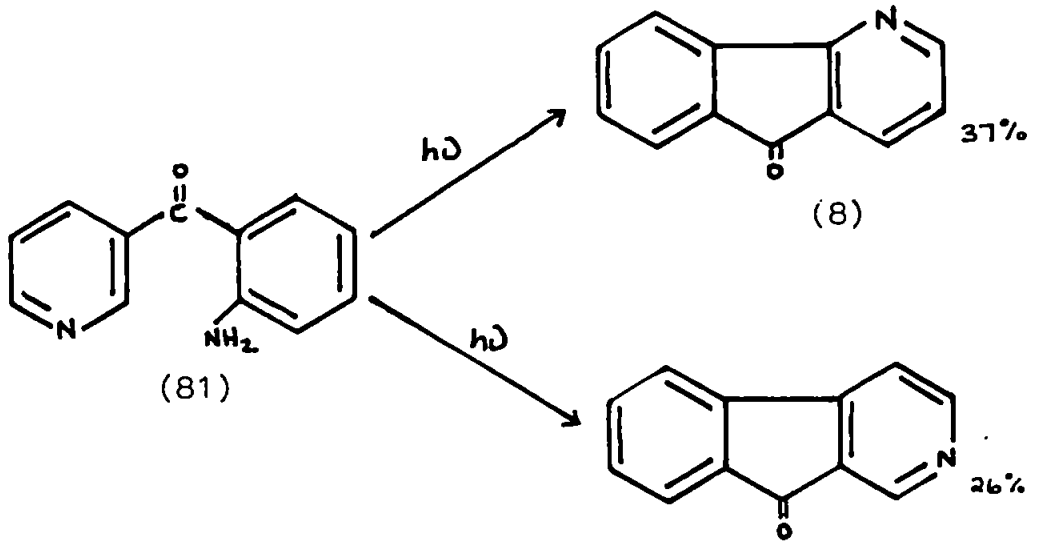
Scheme 46

In 1960, Abramovitch[42] reacted phenyllithium with 3-picoline (78) to give 2-phenyl-3-picoline (79) and 6-phenyl-3-picoline (80). Permanganate oxidation of the major product (79) afforded the acid which was converted via the acid chloride into 5H-indeno[1,2-b]pyridin-5-one (8). Scheme 47.



Scheme 47

In 1963,Abramovitch[43] diazotised 3(2'-aminobenzoyl)-pyridine (81). Decomposition of the diazonium salt in aqueous acid solution gave the indenopyridones (8) and (12). Scheme 48.



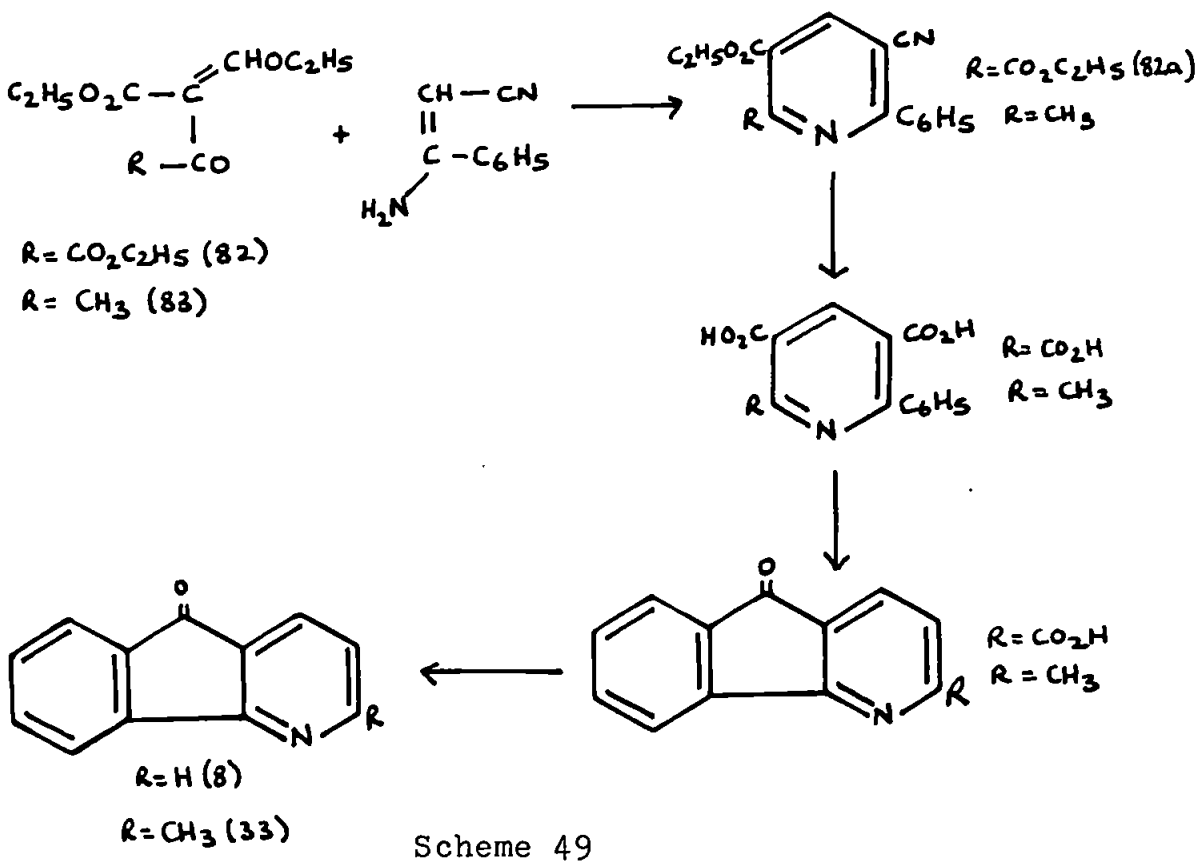
Scheme 48

The methods used by Abramovitch[43] to decompose the diazonium salt are shown below, together with the yield of (8).

Method	(8)%
Thermal	4
Gatterman copper	30
UV	37
Ag powder	2
Fe filings	5
Zn dust	16
Thermal (aq NaOH)	9

The yields of (8) were quite low, the best being obtained with UV light.

Chatterjea and Prasad[44] synthesized 5H-indeno[1,2-b]-pyridin-5-one (8) and 2-methyl-5H-indeno[1,2-b]pyridin-5-one (33) as follows. Diethyl ethoxymethyleneoxalacetate (82) when condensed with 3-amino-3-phenylpropenonitrile in acetic acid readily gave diethyl 3-cyano-2-phenyl-pyridine-5,6-dicarboxylate (82a). The cyanoester gave 5H-indeno[1,2-b]pyridin-5-one (8) via the steps outlined in Scheme 49.

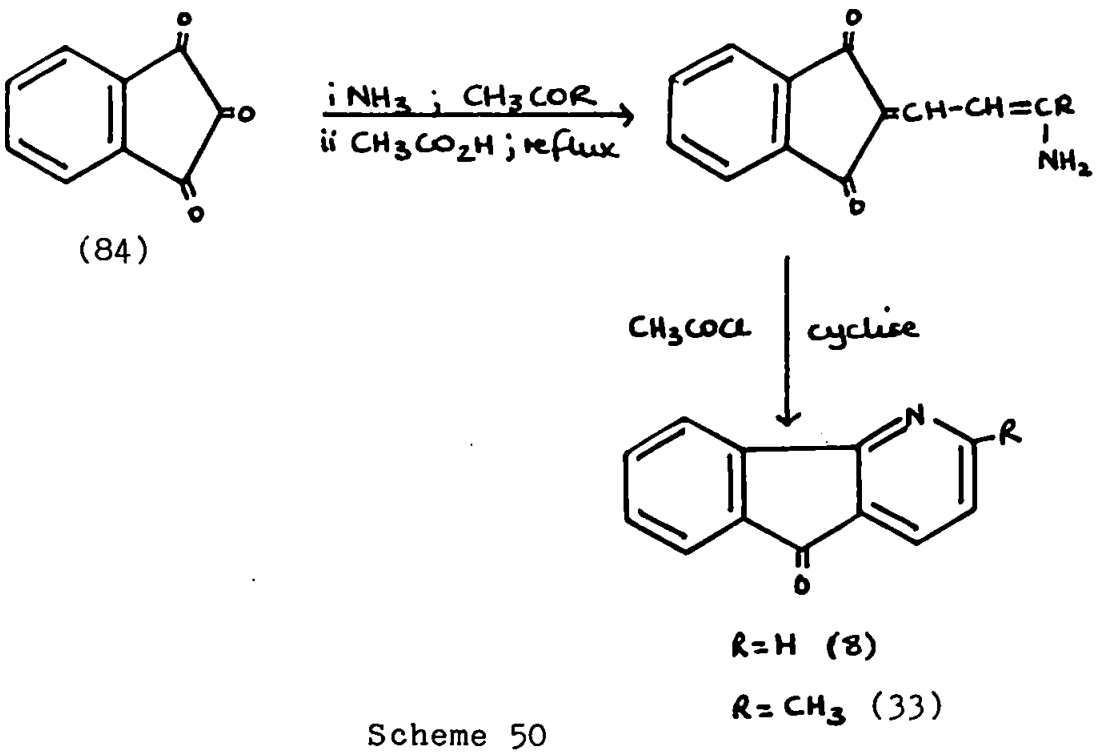


Scheme 49

Similarly 2-methyl-5H-indeno[1,2-b]pyridin-5-one (33) was obtained starting from methyl ethoxymethyleneaceto-acetate (83). Scheme 49.

Type 2. Syntheses involving Construction of a Pyridyl ring.

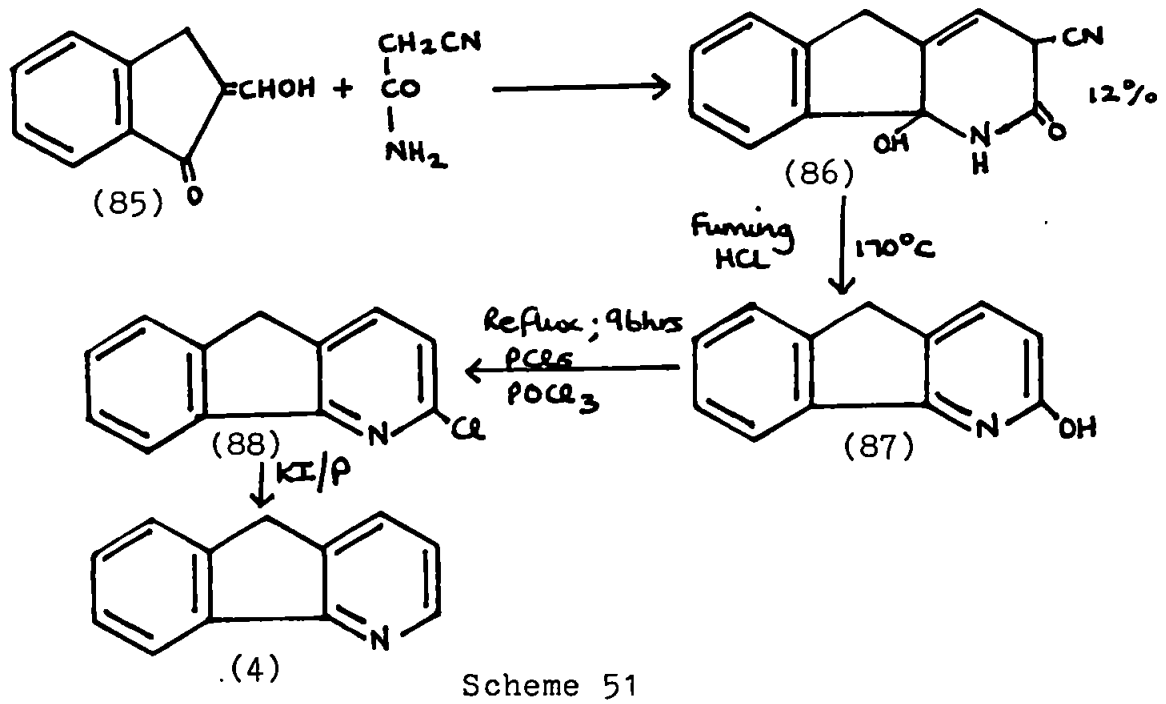
Substituted indanones have provided a useful starting point for the synthesis of the indenopyridine ring system. In an early report, Errera et al[45] prepared 2-methyl-5H-indeno[1,2-b]pyridin-5-one (33) from 1,2,3-indantrione (84). Scheme 50.



(84)

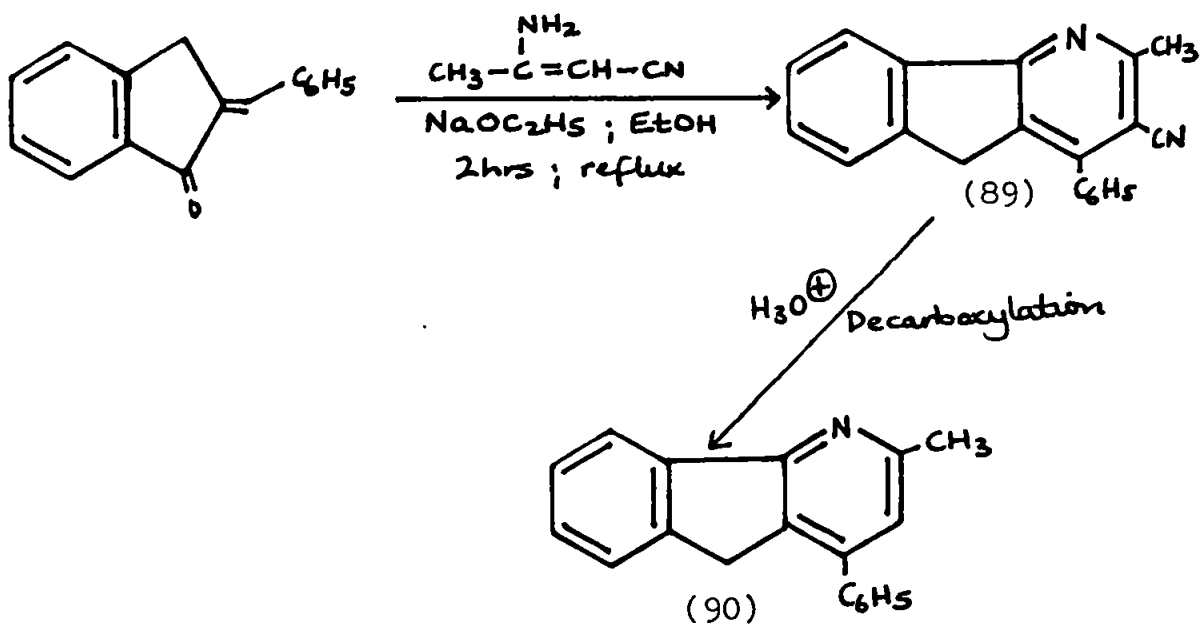
Scheme 50

Chatterjea and Prasad[46] condensed 2-hydroxymethylene-1-indanone (85) with cyanoacetamide at 50-52°C to afford 3-cyano-9b(α)hydroxy-2-oxo-1,3-dihydro-5H-indeno[1,2-b]-pyridine (86) in modest yield. Treatment of (86) with hydrochloric acid at 170°C afforded 2-hydroxy-5H-indeno [1,2-b]pyridine (87), isolated as the chloro-derivative. Reduction of compound(88) with red phosphorus and hydriodic acid gave (4) in poor yield. Scheme 51. Treatment of (86) with HCl in a sealed tube, gave (87) directly in 18% yield.



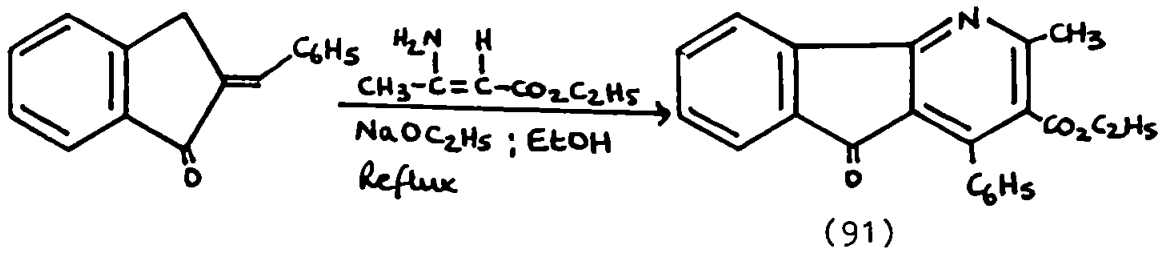
Scheme 51

An alternative synthesis[44] involving the condensation of 2-benzylideneindan-1-one with 3-aminobut-2-enocarbonitrile gave 3-cyano-2-methyl-4-phenyl-5H-indeno[1,2-b]pyridine (89) Subsequent hydrolysis and decarboxylation gave 2-methyl-4-phenyl-5H-indeno[1,2-b]pyridine (90).Scheme 52



Scheme 52

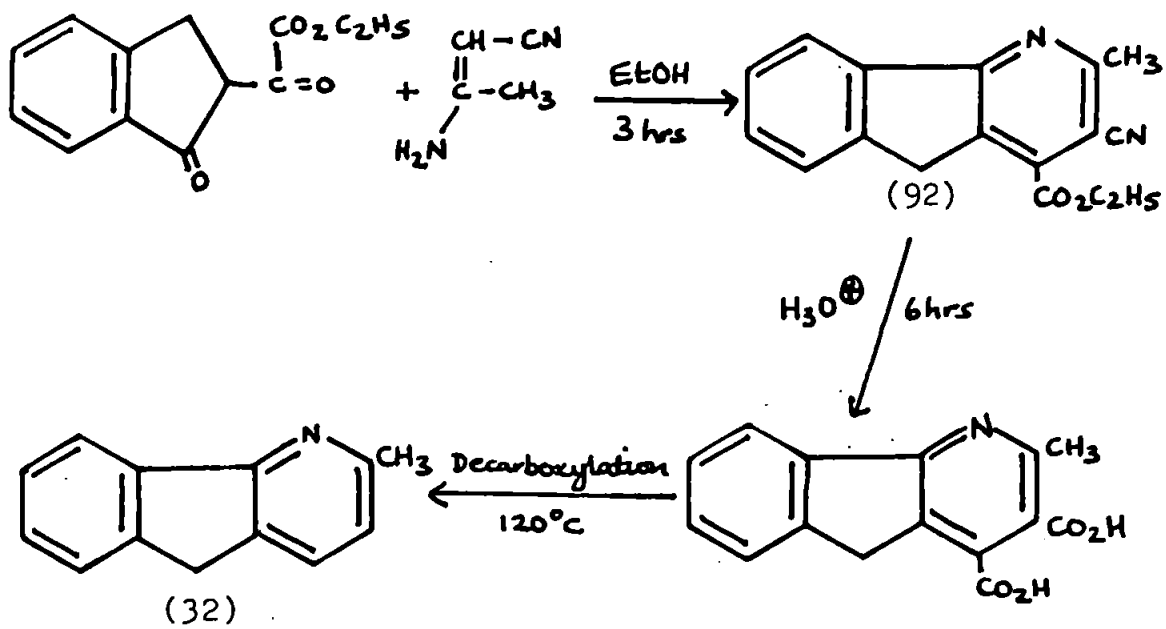
Similarly, with ethyl β-aminocrotonate , ethyl 2-methyl-4-phenyl-5H-indeno[1,2-b]pyridin-5-one carboxylate (91) was obtained.Scheme 53.



(91)

Scheme 53

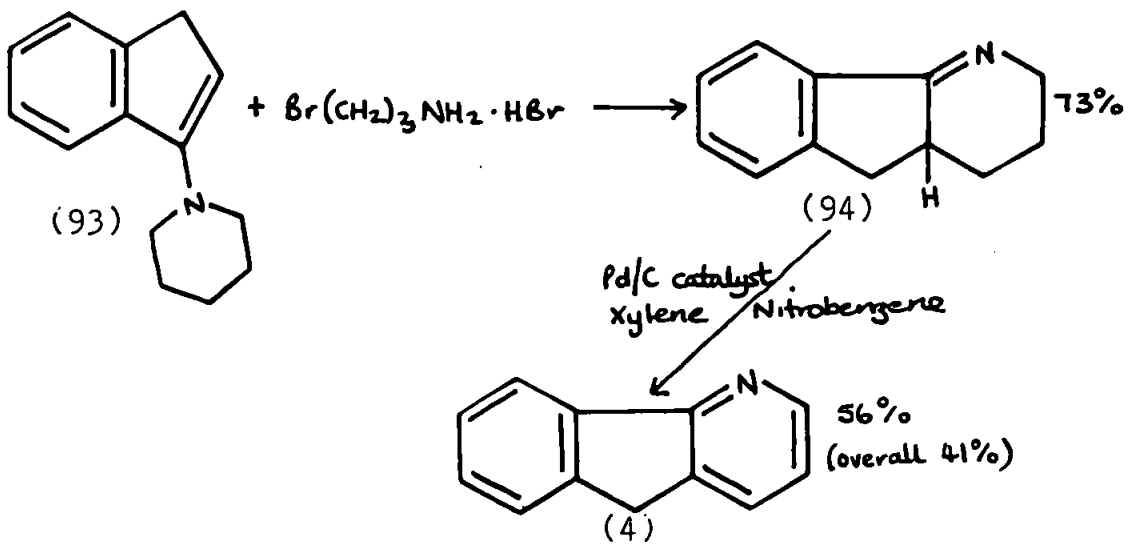
Using a variant of this synthesis, Chatterjea and Prasad [44] condensed ethyl indan-1-one-2-glyoxalate with 3-aminobut-2-enocarbonitrile to give the ester (92) which was converted to 2-methyl-5H-indeno[1,2-b]pyridine (32) by decarboxylation of the di-acid, as shown in Scheme 54.



(32)

Scheme 54

Parcell and Hauck[47] used 1-(N-piperidinyl)indene as starting material to obtain indenopyridine (4). Reaction of the enamine (93) with 3-bromopropylamine-hydrobromide gave the tetrahydro derivative (94) which was dehydrogenated by heating under reflux with nitrobenzene and xylene in contact with a palladium catalyst on carbon to give (4) in 56% yield.Scheme 55

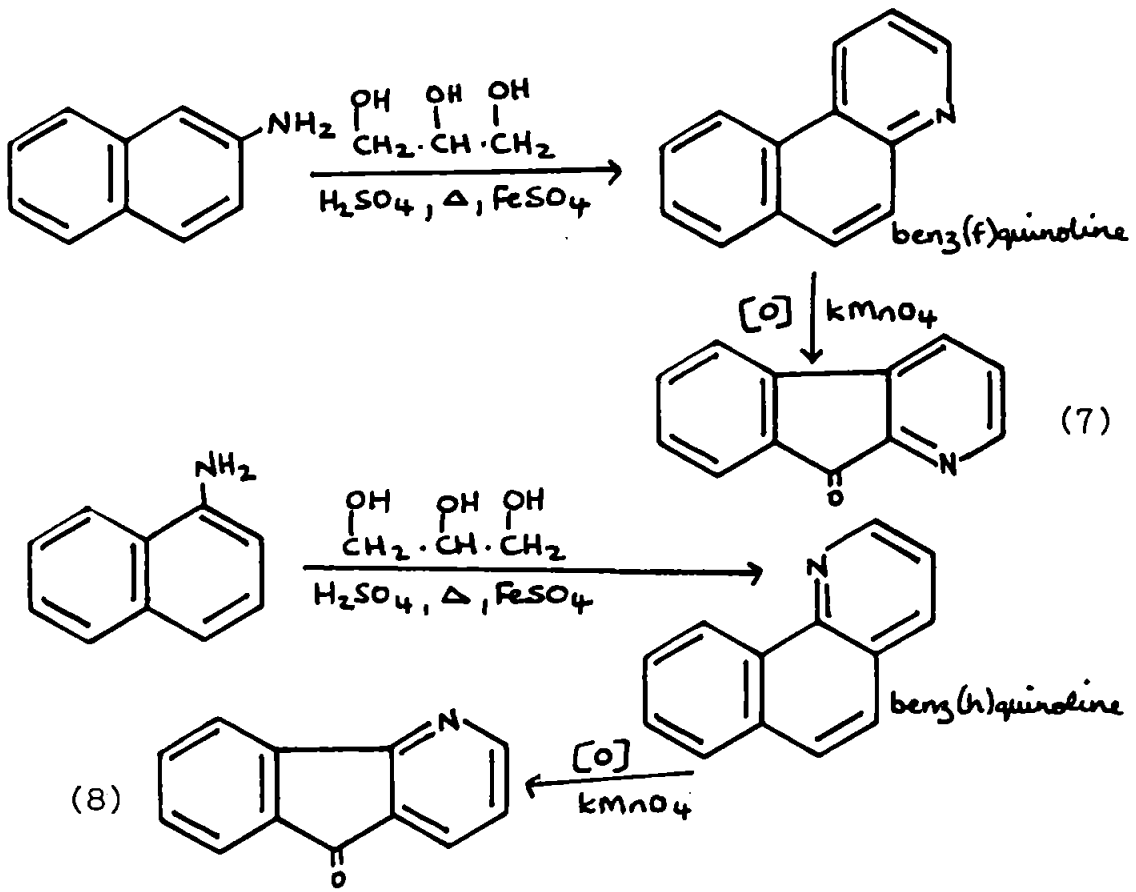


Scheme 55

Type 3. Syntheses involving Ring Contraction of Benzoquinolines.

Three of the four possible isomeric indenopyridines have been prepared from the corresponding benzoquinoline or benzo-isoquinoline.

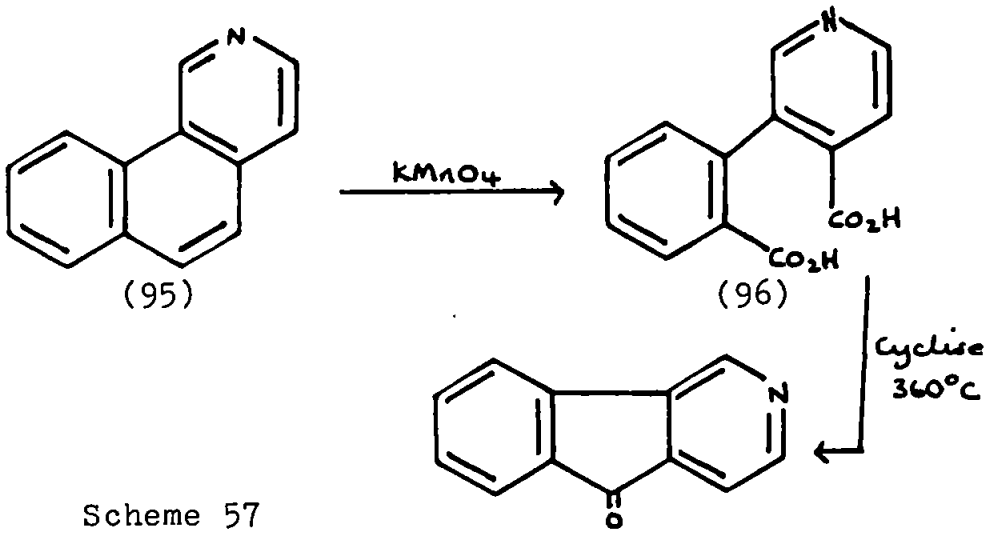
The earliest reported synthesis of an indenopyridine was by Skraup and Coblenz[3] in 1883, they obtained the oxo compounds 9H-indeno[1,2-b]pyridin-9-one (7) and 5H-indeno-[1,2-b]pyridin-5-one (8) by the oxidation of benz[f]quinoline and benz[h]quinoline respectively.Scheme 56.



Scheme 56

Chatterjea and Prasad[48] and Koelsch and Lindquist[49] have used benz[h]isoquinoline (95) as starting material for the synthesis of 5H-indeno[1,2-c]pyridin-5-one (97).

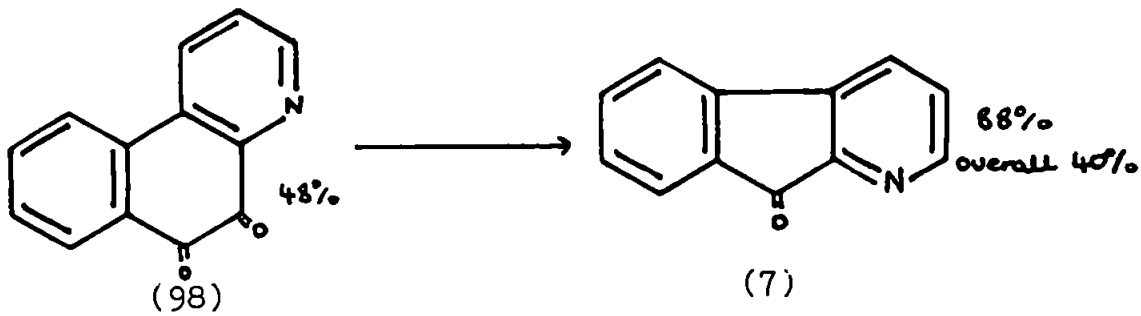
These workers oxidised (95) with potassium permanganate and isolated 3-(carboxyphenyl)-pyridine-4-carboxylic acid (96), which was then pyrolysed at 360°C to give 5H-indeno[1,2-c]pyridin-5-one (97) in low yield (2%). Scheme 57.



(95) (96) (97)

Scheme 57

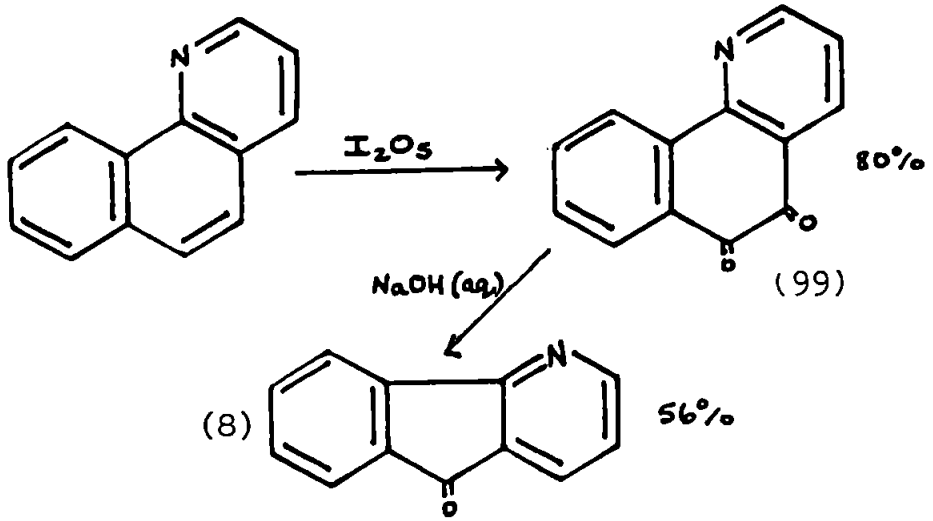
Kloc et al [31] obtained higher yields of indenopyridine by converting the quinoline, using iodine pentoxide as oxidising agent, into the corresponding benz[f]quinolin-9,10-dione (98), which when treated with hot alkali gave 9H-indeno[2,1-b]pyridin-9-one (7) in 40% yield. Scheme 58.



(98) (7)

Scheme 58

In a similar way, these workers prepared 5H-indeno[1,2-b]-pyridin-5-one (8) in 56% yield from benz[h]quinolin-5,6-dione (99). Scheme 59.

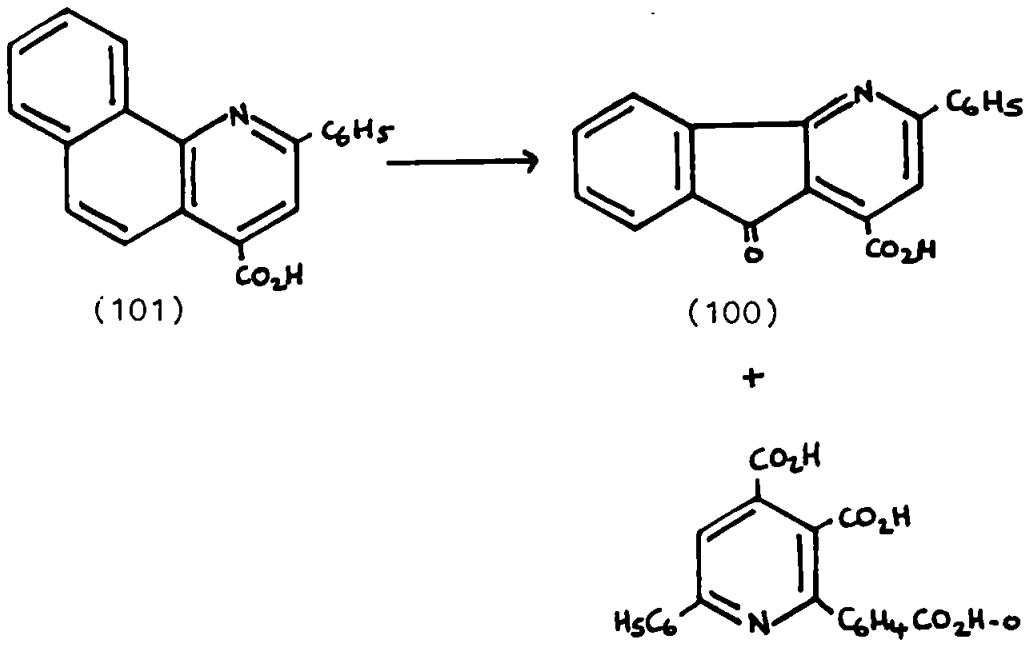


(99) (8)

Scheme 59

It is probable that the step using hot alkali proceeds via a benzil-benzillic acid rearrangement, accompanied by subsequent decarboxylation and oxidation.

A small quantity of 2-phenyl-5H-indeno[1,2-b]pyridin-5-one-4-carboxylic acid (100) was formed together with 2(o-carboxyphenyl)-6-phenylpyridine-3,4-dicarboxylic acid by oxidation of 2-phenylbenzo[h]quinoline-4-carboxylic acid (101).Scheme 60.



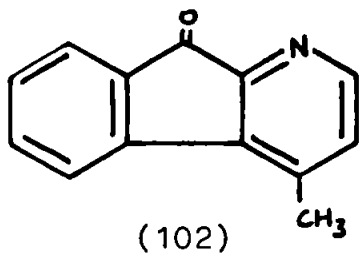
Scheme 60

10-Azafluoranthene (9), isolated by fractional distillation of coal-tar pitch, can be oxidised to give a mixture of 5H-indeno[1,2-b]pyridin-5-one-6-carboxylic acid (10) and 9H-indeno[2,1-b]pyridin-9-one-8-carboxylic acid (11). Decarboxylation of the carboxylic acids (10 and 11) gave (8) and (7) respectively,[50] as described earlier in Chapter 2,Scheme 1, page 4.

Chapter 5. Naturally Occurring Indenopyridines.

It was not until very recently that indenopyridines were found to occur naturally. To date, only 11 indenopyridine derivatives have been isolated , mostly from the Annonaceae family. This is a large family of trees with approximately 130 genera and 2300 species. Phytogeographically, they occur entirely in tropical and sub-tropical regions.

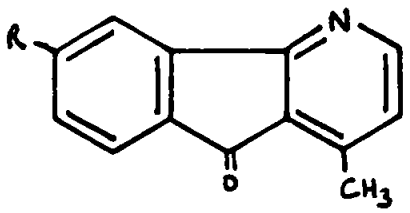
The first naturally occurring indenopyridine was isolated in small quantities in Manaus ,Brazil in 1976. The trunk wood of Onychopetalum amazonicum was found to contain an alkaloid called Onychine[11] .This compound was originally thought to be 4-methyl-9H-indeno[2,1-b]-pyridin-9-one (102).

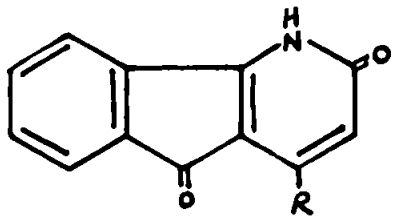


(102)

However, subsequent work showed that this structure was incorrect. N.M.R. studies of Onychine isolated from Cleistopholis patens and Guatteria dielsiana by Tédic[51] et al, and a number of syntheses[52,53,54] have shown that Onychine is in fact 4-methyl-5H-indeno[1,2-b]pyridin-5-one (26). The initial assignment of an incorrect structure to Onychine has led to some confusion in the literature. For example, compound (103) which was isolated by Goulart[52] et al, from Guatteria dielsiana was originally thought to be 6-methoxyOnychine (4-methyl-6-methoxy-9H-indeno[2,1-b]-pyridin-9-one) but is in fact 4-methyl-8-methoxy-5H-indeno[1,2-b]pyridin-5-one (103)

The correct structures of dielsine (104) and dielsinol (105) also isolated from Guatteria dielsiana by Goulart[52] et al are 4-methyl-2-oxo-1,2-dihydro-5H-indeno[1,2-b] pyridin-5-one and 4-hydroxymethyl-2-oxo-1,2-dihydro-5H-indeno[1,2-b]-pyridin-5-one respectively.





26 R=H

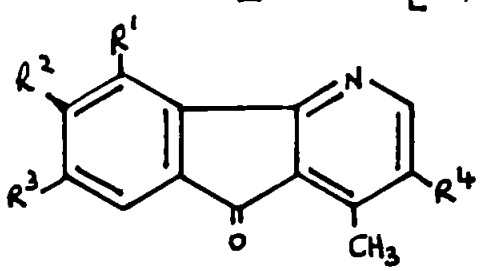
103 R=OCH_3

104 R=CH_3

105 R=CH_2OH

Tédic[51] also isolated the above alkaloids 103,104 and 105, from Meiogyne virgata and Oxandra cf. major.

At the same time , Zhang et al[54] isolated three novel alkaloids from Oxandra xylopiodoes. These were shown to be 6-hydroxyonychine (4-methyl-8-hydroxy-5H-indeno[1,2-b]-pyridin-5-one),(106) . 5-hydroxy-6-methoxyonychine or 4-methyl-8-methoxy-9-hydroxy-5H-indeno[1,2-b] pyridin-5-one (107) and 2,6-dimethoxy-7-hydroxyonychine or 4-methyl-3,8-dimethoxy-7-hydroxy-5H-indeno[1,2-b]pyridin-5-one (108).

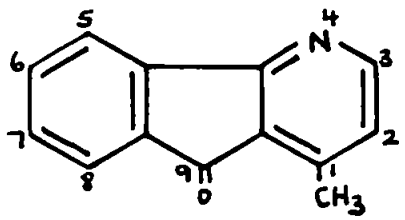


R^1=R^3=H, R^2=OH ,R^4=H (106)

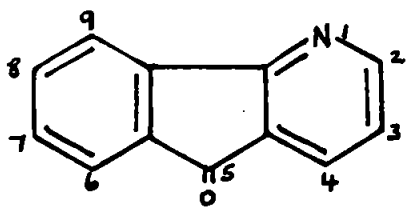
R^1=OH, R^2=OCH_3, R^3=R^4=H (107)

R^1=H, R^2=OCH_3,R^3=OH, R^4=OCH_3 (108)

There is some confusion over the naming of these compounds, the trivial name Onychine, has a different series of locant numbers compared to the indenopyridine . The numbering system for Onychine and 5H-indeno[1,2-b]pyridin-5-one (8) are shown below, and should eliminate any confusion.



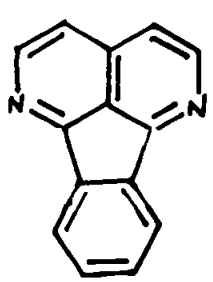
Onychine (26)



5H-indeno[1,2-b]pyridin-5-one
(8)

In 1987 , Huffords studies [55] of the stem and root bark of Cleistopholis patens led to the isolation of several sesquiterpenes and alkaloids.

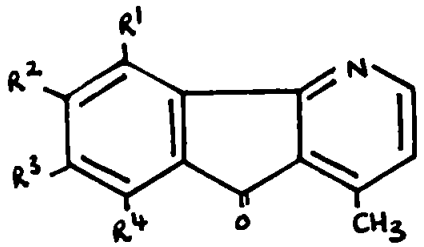
The alcoholic extracts of C.patens showed significant anticandidal activity , isolation of the active component gave eupolauridine (28) whose identity was confirmed by comparison with authentic sample, which was synthesized using the method of Bowden.[22]



(28)

Eupolauridine (28) was synthesized and the synthetic intermediates were evaluated for anticandidal activity. One of the intermediates which was found to be active was Onychine (26).(26) was found to be comparable to (28) in its anticandidal activity. Both are considered as promising potential new antifungal drugs.

Laprevote[53] in 1988 isolated 5 new alkaloids from the trunk bark of Unonopsis spectabilis , 4 of which had been isolated previously from Annonaceae .These are Onychine (26), 6-hydroxyonychine (106), macondine (109) and ursuline (110).The only novel compound isolated was isoursuline (111) whose structure was determined together with that of (110).



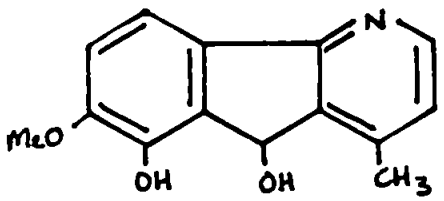
$R^1=R^2=H$, $R^3=OH$, $R^4=OCH_3$ (109)

$R^1=OCH_3$, $R^2=OH$, $R^3=R^4=H$ (110)

$R^1=OH$, $R^2=OCH_3$, $R^3=R^4=H$ (111)

Prior to 1989, all the indenopyridine derivatives mentioned have been isolated from the family Annonaceae, eg, Cleistopolis patens , Guatteria dielsiana , Oxandra xylopioides , Onychopetalum amazonicum and Meigyne virgata.

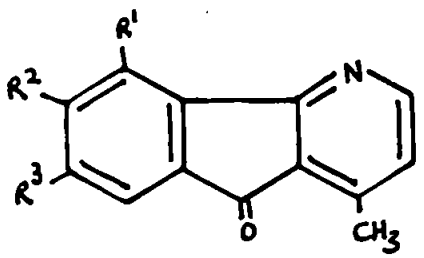
However, in this year , Wu et al[56] isolated the novel alkaloid - polylongine (112) - from the leaves of Polyalthia longifolia, a genus containing at least 120 species.



(112)

The isolation of polylongine (112) is the first report of an indenopyridine alkaloid from the genus Polyalthia.

Chakrabarty and Patra[57] in 1990, also isolated 3 indeno-pyridine alkaloids from the bark of Polyalthia longifolia Thw., By spectral analysis, these have been identified as Onychine (26), Darienine (113) and 6,7-dimethoxyonychine (114).



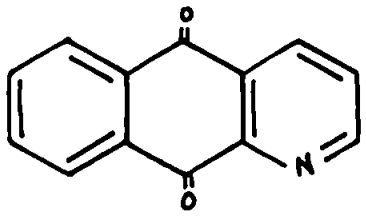
$R^1=R^2=OCH_3$, $R^3=OH$ (113)

$R^1=H$, $R^2=R^3=OCH_3$ (114)

This is the second isolation of Darienine from a natural source, it was first isolated by Arango[58] in 1987 from the trunk bark of Oxandra cf. major. Compound (114) is a novel alkaloid.

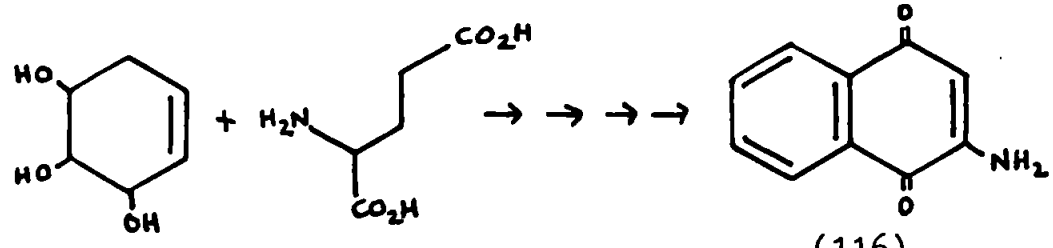
The Biosynthesis of Onychine.

The co-occurrence of 5H-indeno[1,2-b]pyridin-5-one (8) and benz[g]quinoline-5,10-dione (115) in Guatteria dielsiana and Cleistopholis patens led Goulart [52] to suggest a biogenetic relationship between them, based on a shikimate-acetate pathway,



(115)

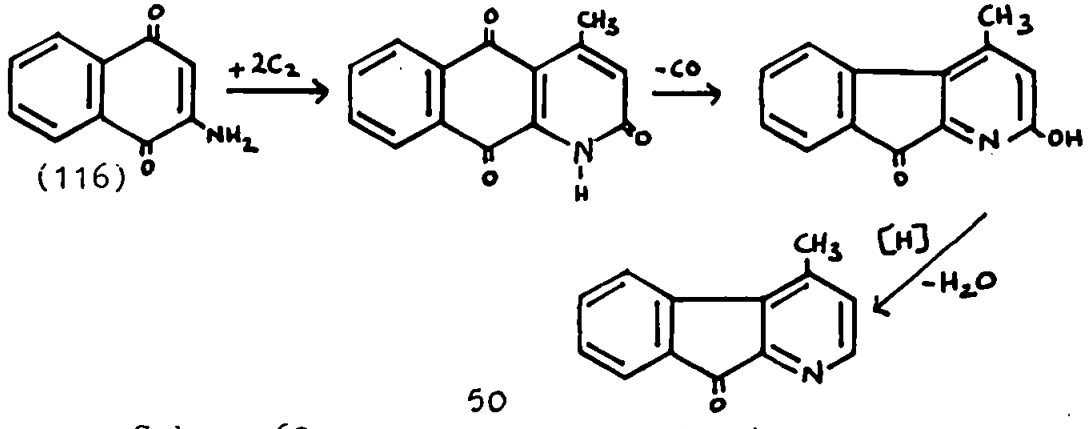
Goulart [52] proposed that the reaction between shikimate and glutamic acid gave a 2-aminonaphthoquinone intermediate (116), by analogy with the biosynthesis of benzoquinolin-diones. Scheme 61.



(116)

Scheme 61

By analogy with the biosynthesis of nibomycin [59], a metabolite from Streptomyces sp., 4-methyl-9H-indeno[1,2-b]-pyridin-9-one (102) may be obtained via the following route. Scheme 62.

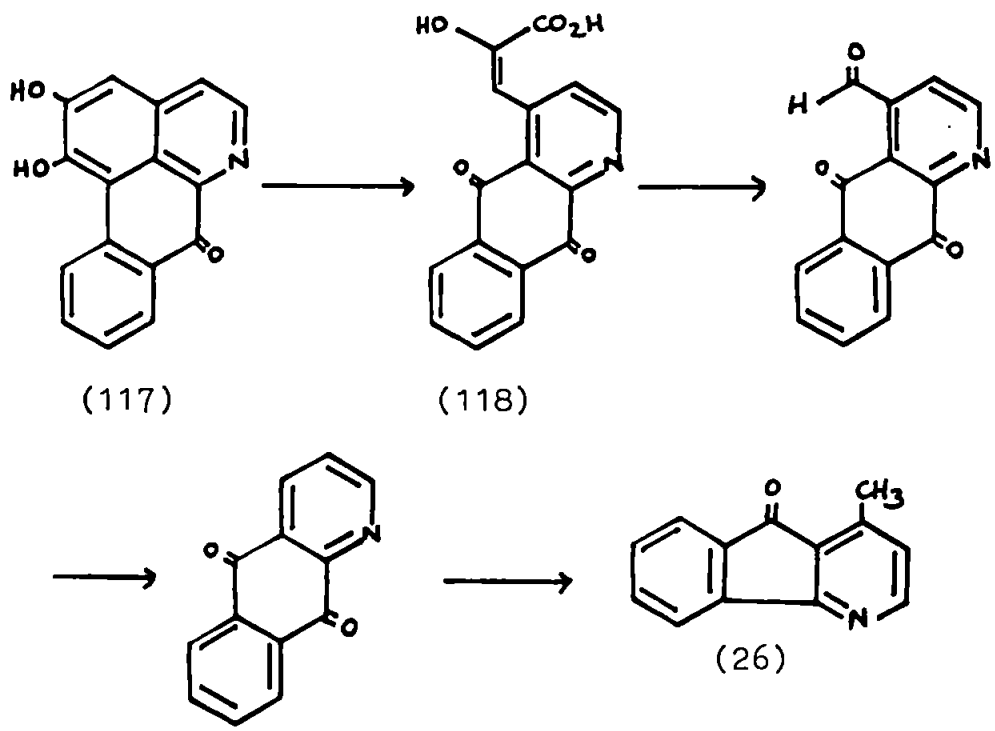


(116) (102)

Scheme 62

A similar pathway was proposed by Waterman [60] and Cavé et al.[61] These hypothetical pathways were suggested before it was realised by Tádic [51] that the structure of Onychine was 4-methyl-5H-indeno[1,2-b]pyridin-5-one (26) and not 4-methyl-9H-indeno[1,2-b]pyridin-9-one (102). The proposed route, which has been suggested above, was therefore no longer viable.

Whilst studying Meigyne virgata in 1987 , Tadic[51] proposed that Onychine (26) could be related to the diazafluoranthene - eupolauridine (28)- through a common hypothetical percursor derived from the oxoaporphine - liriodenine (117). It was suggested that (117) may undergo an extradiol cleavage giving the anthraquinone acid (118),which can then be converted to Onychine (26) as shown in Scheme 63.



(117) (118) (26)

Scheme 63.

Chapter 6. Later Indenopyridine Syntheses.

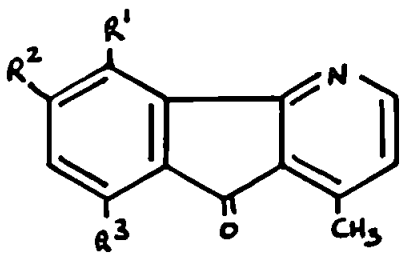
This chapter is presented in two parts. The first part will deal with the specific synthesis of Onychine (26) and its derivatives. The second half of the chapter deals with the general syntheses of indenopyridines from 1975.

Synthetic Routes to Onychine and its Derivatives,

Before the work of Tadic [51] et al and Zhang et al [54], the structure of Onychine was uncertain.

Zhang et al [54] produced several 5H-indeno[1,2-b]pyridin-5-ones via phenylnicotinic acids in order to establish the structures of the compounds he had isolated.

Syntheses provided 3 additional related compounds- 5,6-dimethoxyonychine (119), 8-hydroxyonychine (120) and 5,8-dimethoxyonychine (121).

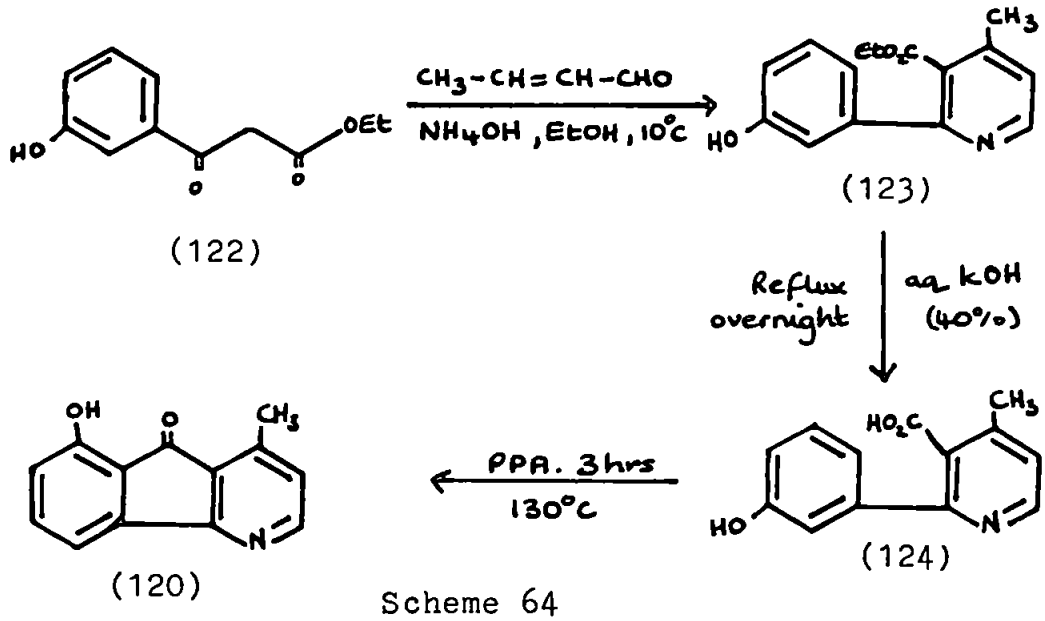


$R^1=R^2=OCH_3$, $R^3=H$ (119)

$R^1=R^2=H$, $R^3=OH$ (120)

$R^1=R^3=OCH_3$, $R^2=H$ (121)

Zhang et al [54] obtained the alkaloid (120) in the following manner. Scheme 64.

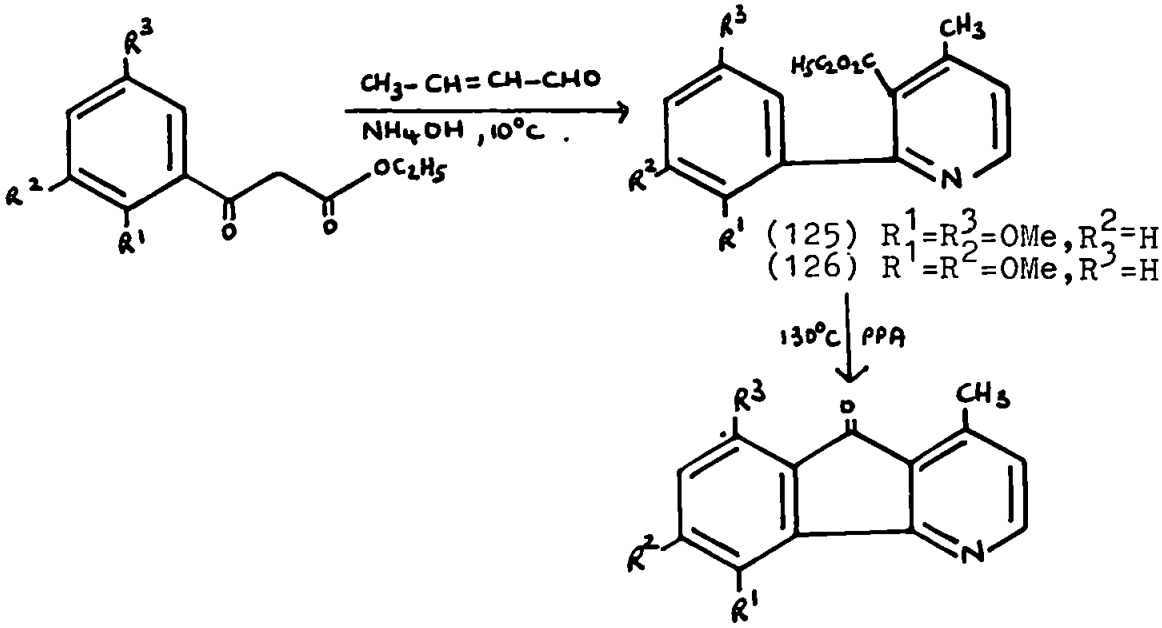


(122) (123) (124) (120)

Scheme 64

Reaction of the ester (122) with crotonaldehyde overnight afforded ethyl 2(3-hydroxyphenyl)-4-methyl-nicotinate (123). The nicotinate was refluxed with aqueous potassium hydroxide (40%) overnight and the resulting solution was concentrated and purified on a silica column to afford 2(3-hydroxy-phenyl)-4-methyl-nicotinic acid (124). Cyclisation of (124) with polyphosphoric acid afforded two products - 6-hydroxyonychine (106) and 8-hydroxyonychine (120).

In a similar manner 5,8-dimethoxyonychine (121) and 5,6-dimethoxyonychine (119) were prepared from ethyl 2(2,5-dimethoxyphenyl)-4-methyl-nicotinate (125) and ethyl 2(2,3-dimethoxyphenyl)-4-methyl-nicotinate, (126) respectively as shown in Scheme 65.

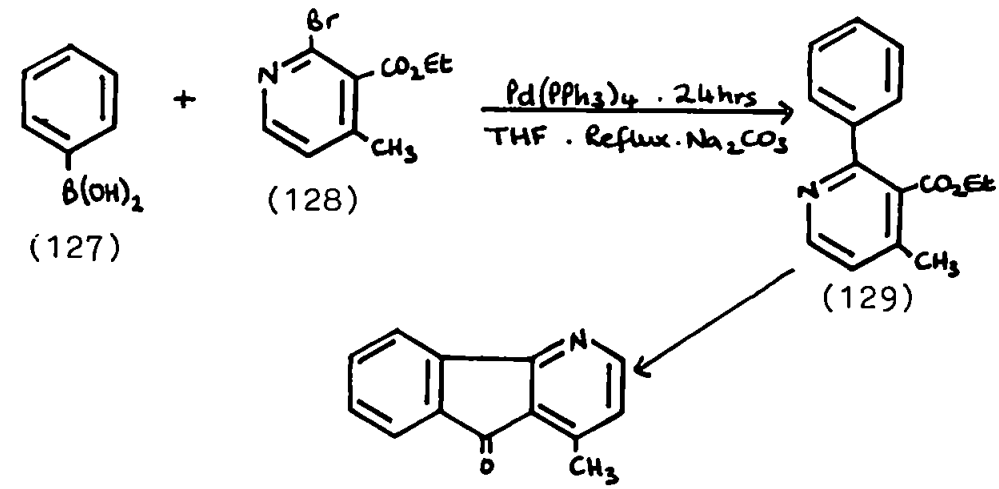


(121) $R^1=R^3=OMe$, $R^2=H$
(119) $R^1=R^2=OMe$, $R^3=H$

Scheme 65

In 1988, Alves[62] synthesized Onychine (26) and 6-methoxyonychine (102) by Pd(0)-catalysed cross coupling of arylboronic acids and arylstannane with bromonicotinate ester.

Commercial phenylboronic acid (127) was coupled with the readily available bromonicotinic ester (128) using a $Pd(PPh_3)_4$ catalyst to give ethyl 4-methyl-2-phenyl-3-pyridine carboxylate (129), which was then cyclised with polyphosphoric acid to give Onychine (26).Scheme 66.

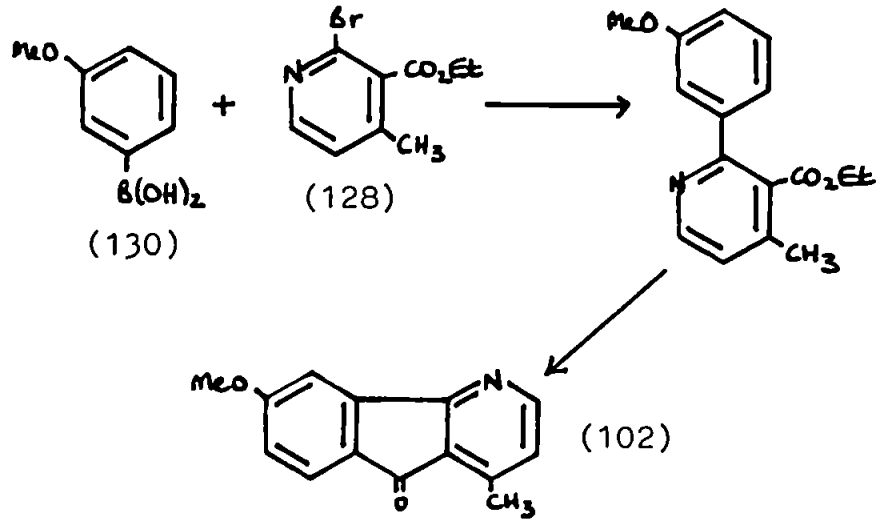


(127) (128) (129)

(26)

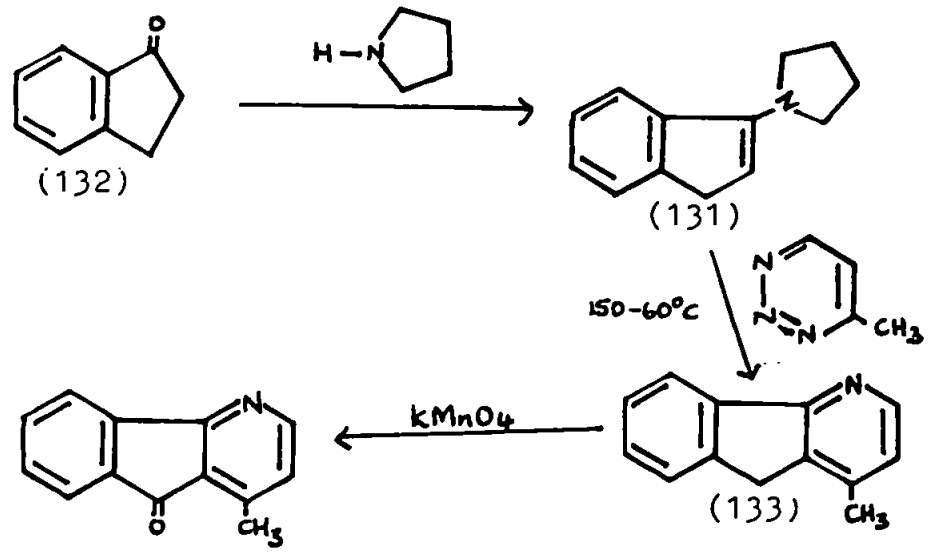
Scheme 66

In a similar way, starting from m-methoxyphenylboronic acid (130), 6-methoxyonychine (102) was obtained.Scheme 67.



Scheme 67

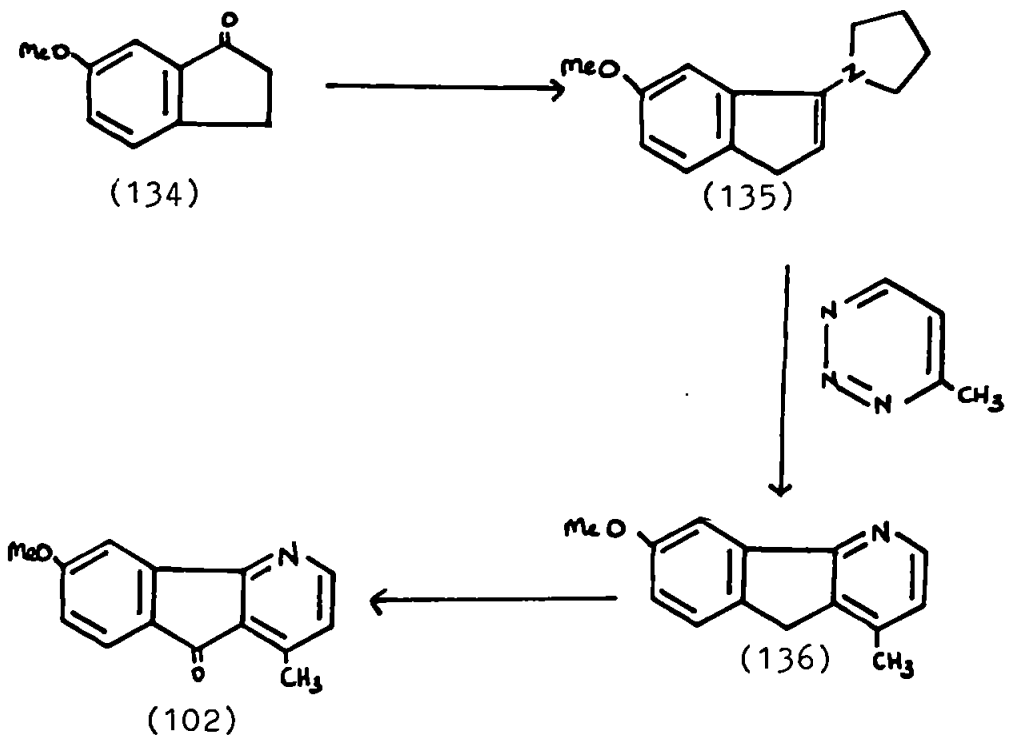
Also in 1988, Okatani [63] et al synthesized Onychine (26) according to the following reaction scheme,Scheme 68.



Scheme 68

Diels-Alder reaction of pyrrolidine enamine (131) of 1-indanone (132) with 4-methyl-1,2,3-triazine in dry o-dichlorobenzene in a sealed glass tube at 150-60°C gave 4-methyl-5H-indeno[1,2-b]pyridine (133). Oxidation of (133) with potassium permanganate afforded Onychine (26).

Okatani [63] also synthesized 6-methoxyonychine (102) starting from 6-methoxyindanone (134).Scheme 69.

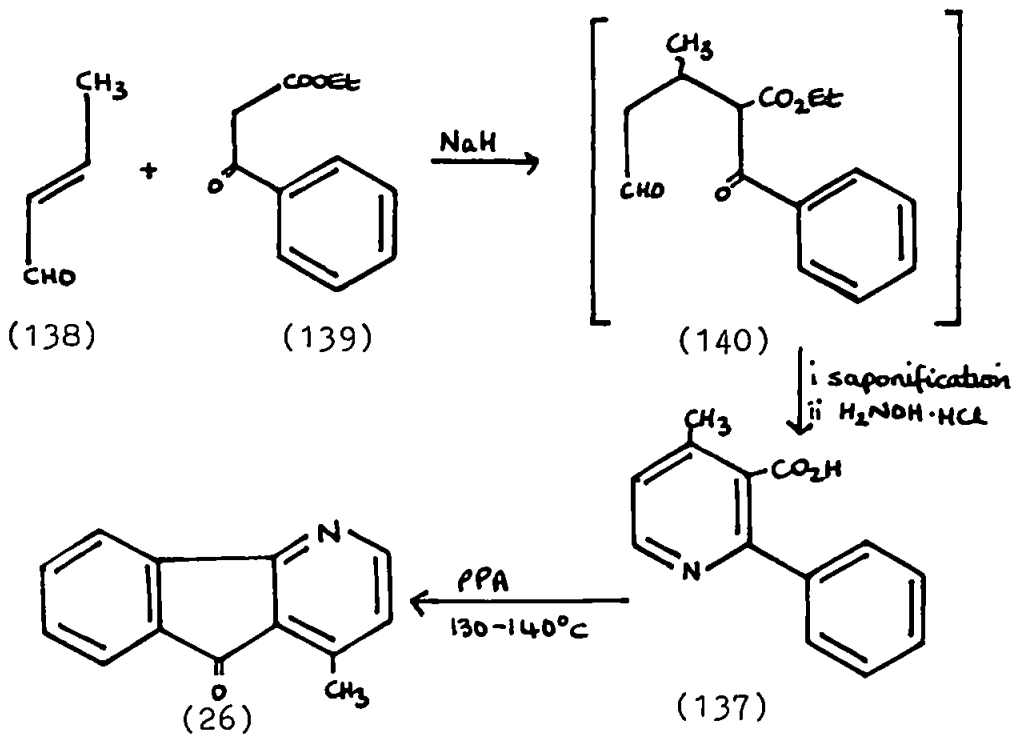


Scheme 69

Treatment of (134) with pyrrolidine and cyclo-addition reaction of the enamine (135) as above gave 8-methoxy-5H-indeno[1,2-b]pyridine (136), which on oxidation afforded (102) .Scheme 69.

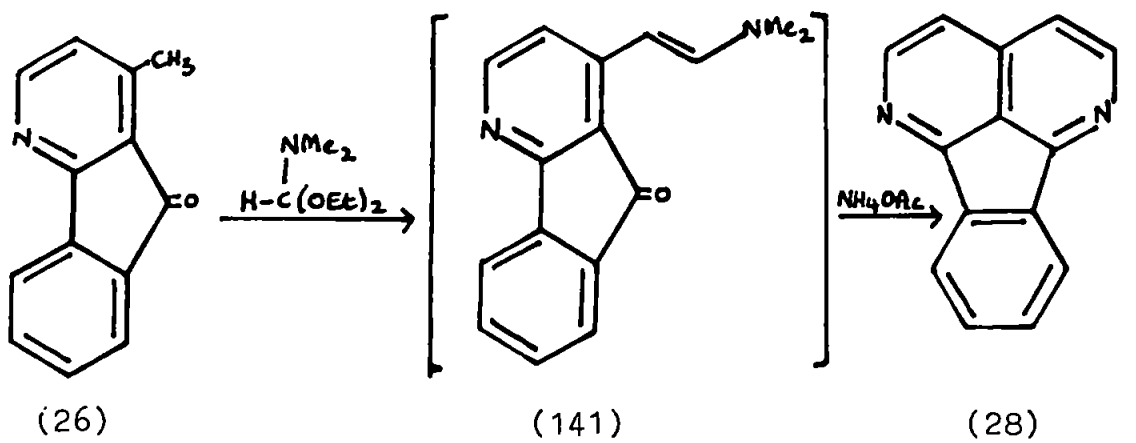
In 1989, Bracher[64] improved the total synthesis of onychine (26) by using a new approach to the preparation of the biaryl (137).

The base-catalysed Michael-addition of crotonaldehyde (138) to the β-keto ester (139) gave the intermediate (140) which on reaction with hydroxylamine.hydrochloride gave the biaryl (137).Cyclisation of (137) afforded Onychine (26). Scheme 70.



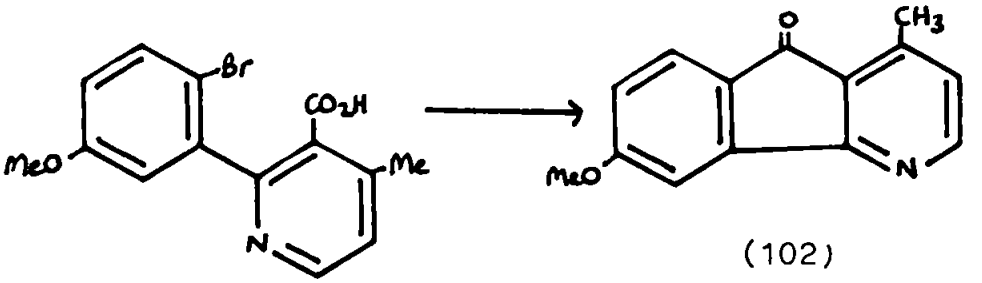
Scheme 70

It is known [55] that Onychine (26) is one of the intermediates in the formation of eupolauridine (28). Bracher [64] synthesised (28) from (26) in a one-pot synthesis via the enamine (141). Reaction of onychine (26) with dimethylformamide-diethylacetal gave the enamine (141), treatment of (141) with ammonium chloride and ammonium acetate afforded eupolauridine (28). Scheme 71.



Scheme 71

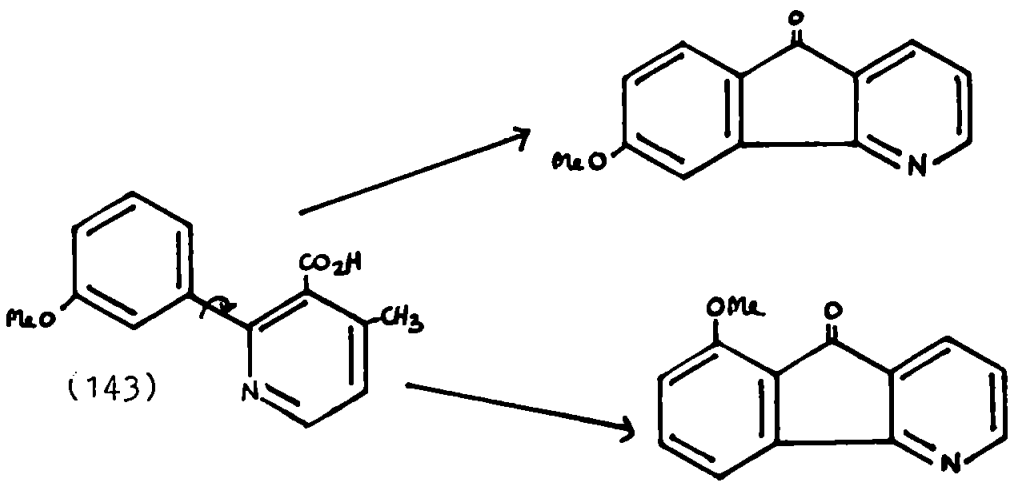
More recently, Bracher [65] obtained 6-methoxyonychine (102) regioselectively from the biaryl 2(2-bromo-5-methoxy-phenyl) -4-methyl-3-pyridinecarboxylic acid (142) via a Parham-type cyclisation.Scheme 72.



(142) (102)

Scheme 72

Bracher [65] used this new strategy for the synthesis of indenopyridines with predictable substitution patterns. The ring system was built by cyclisation of the appropriate aryl pyridinecarboxylic acid. However, biaryl (143) with unsymmetrical substitution in the benzene ring gave a mixture of isomers upon cyclisation.Scheme 73.

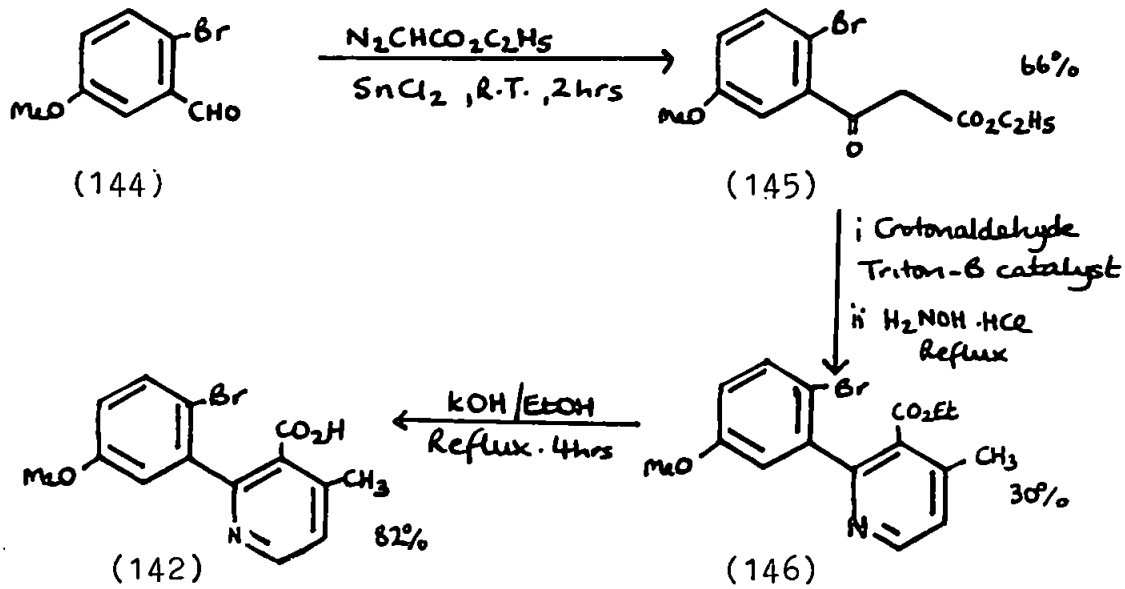


(143)

Scheme 73

To overcome this problem the following reaction scheme was followed.

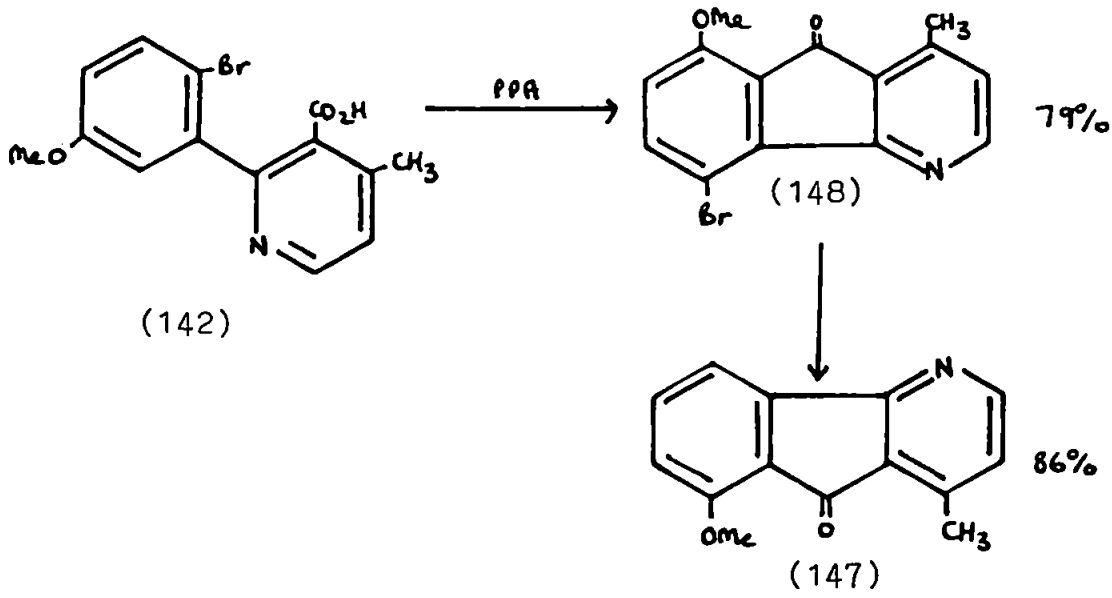
2-Bromo-5-methoxybenzaldehyde (144) was converted to the β-keto ester (145) by Roskamp's one-step synthesis using ethyl diazoacetate and tin(II)chloride. Michael addition of crotonaldehyde to (145), followed by heating the product with hydroxylamine.hydrochloride gave the aryl pyridine ester (146).Scheme 74.



Scheme 74

Saponification of the ester (146) led to the intermediate biaryl (142), which was then converted to either pure 6-methoxyonychine (102) or 8-methoxyonychine (147) by the choice of reaction conditions.

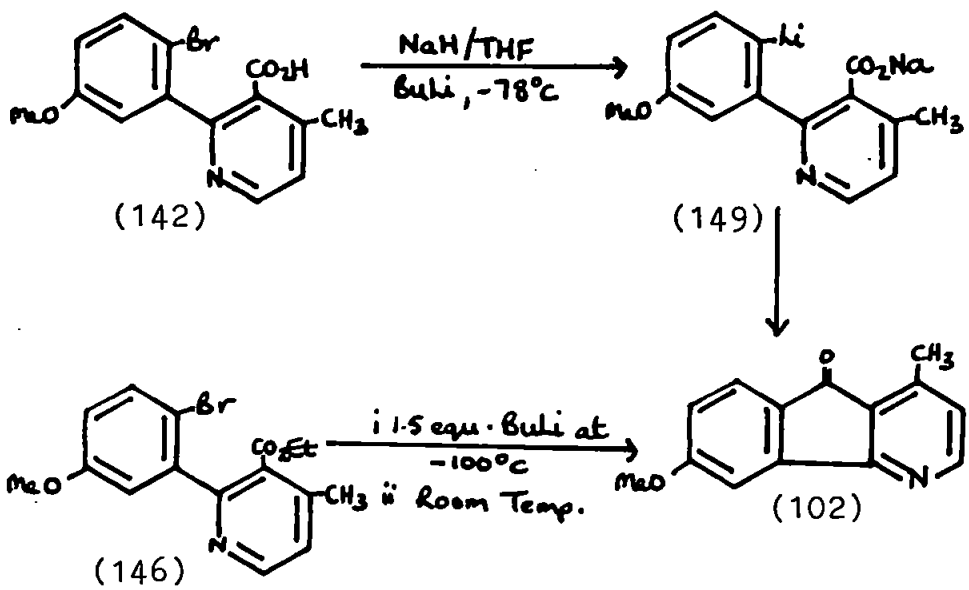
Cyclisation of (142) with PPA gave the bromo,methoxy-indenopyridine (148).The bromine atom,which was acting as a blocking group for one of the possible two sites for cyclisation in this reaction, was removed by catalytic hydrogenation to give pure 8-methoxyonychine (147). Scheme 75.



Scheme 75

Alternatively, treatment of (142) with one equivalent of sodium hydride followed by halogen-metal exchange with butyl lithium at -78°C gave, via an intermediate organo-metallic species (149), 6-methoxyonychine (102) in 40% yield.

Alternatively, direct cyclisation of the bromo-ester (146) was achieved by treatment with 1.5 equivalents of butyl lithium at -100°C. Warming the reaction mixture to room temperature gave (102) in 30% yield. Scheme 76.



Scheme 76

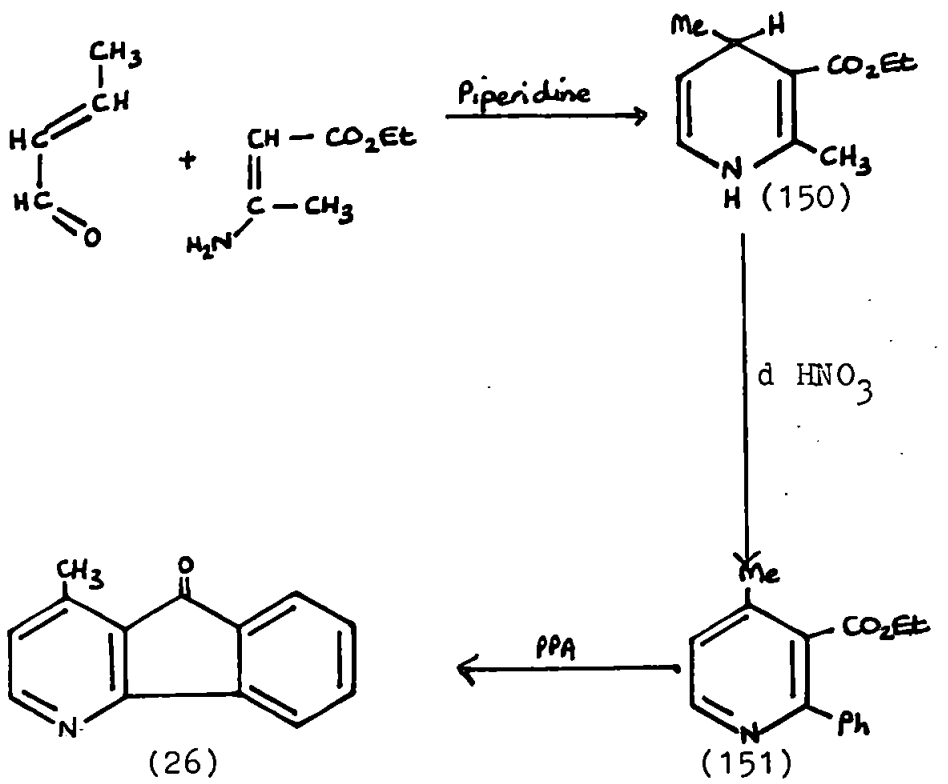
This was the first example of the formation of an indenopyridine ring system by the use of the Parham cyclisation strategy.

General Indenopyridine Synthesis.

Type 1. Syntheses involving formation of a Cyclopentane ring.

In 1976, Bowden et al [22] used a Hantzsch synthesis for the production of 4-methyl-5H-indeno[1,2-b]pyridin-5-one (26)

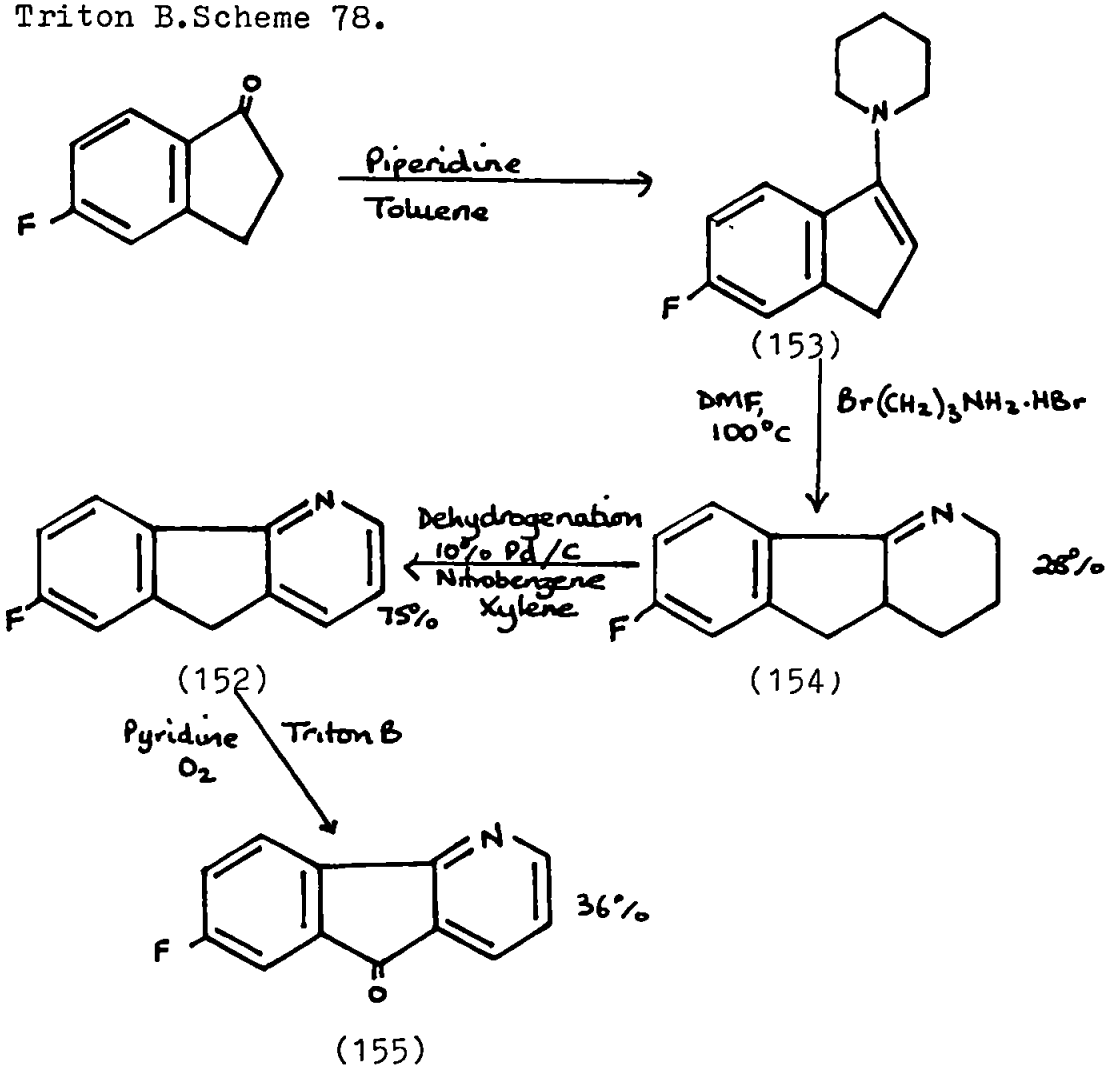
Condensation of crotonaldehyde with ethyl 3-aminocrotonate in the presence of piperidine gave the dihydropyridine derivative (150) which on oxidation with dilute nitric acid afforded the pyridine (151).Cyclisation of (151) with polyphosphoric acid then afforded (26).Scheme 77.



Scheme 77.

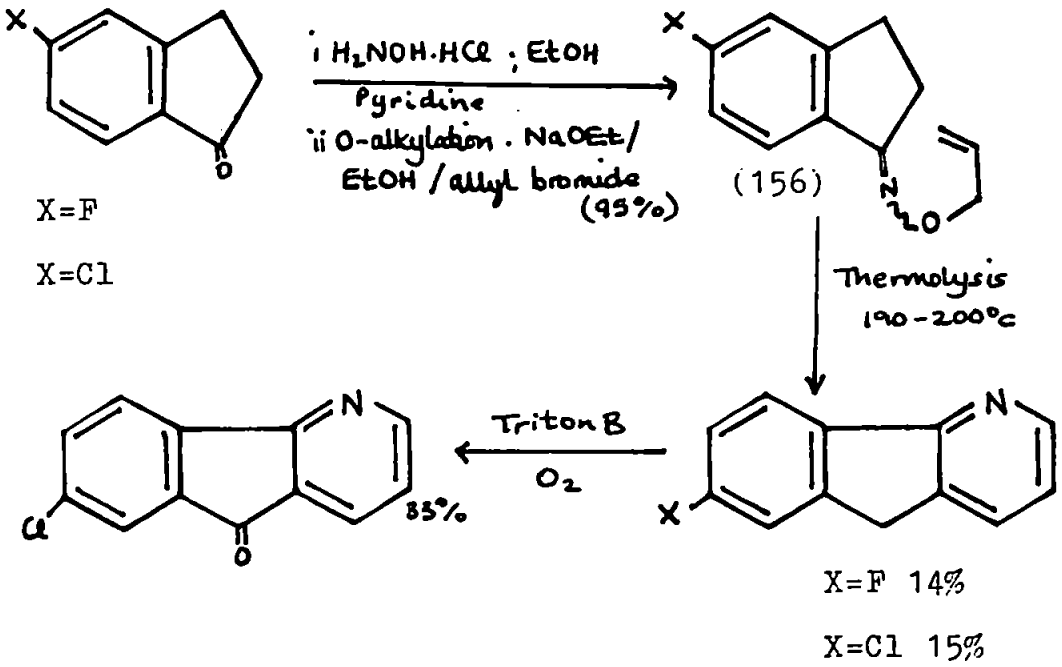
DuPriest et al[24] prepared indenopyridines using a relatively low cost synthesis. Using a method based on Parcell and Hauck's synthesis[47], DuPriest[24] prepared 7-fluoro-5H-indeno-[1,2-b]pyridine (152) from 1-indanone (132).

The piperidine enamine of 5-fluoro-1-indanone(153) was reacted with 3-bromo-propylaminehydrobromide to yield a tetrahydroindenopyridine (154) which was then dehydrogenated to give the desired indenopyridine (152).This was oxidised to 7-fluoro-5H-indeno[1,2-b]pyridin-5-one (155) by bubbling oxygen in a pyridine solution of (152) with Triton B.Scheme 78.



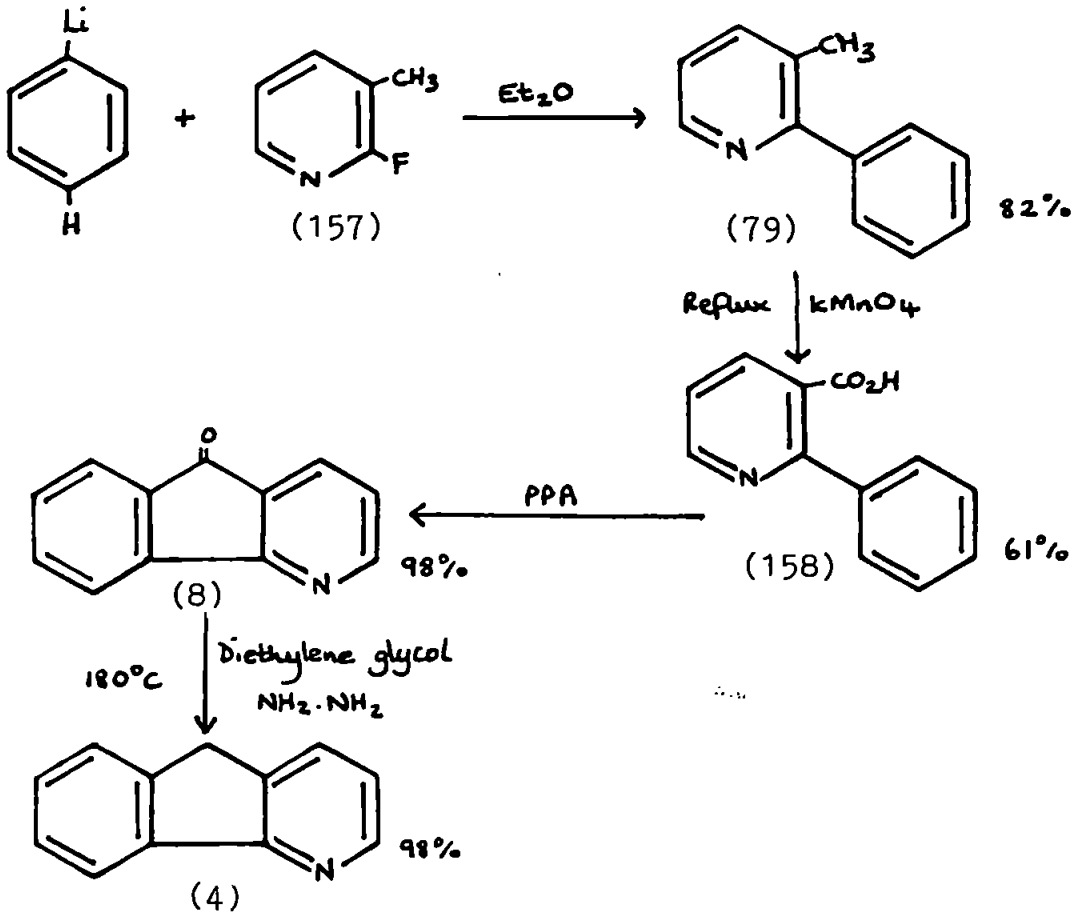
Scheme 78

A second route from 5-halo-1-indanones investigated by DuPriest [24] was based on Irie's synthesis [66] of substituted pyridines from the thermolysis of O-allyl oxime ethers. Both 5-fluoro- and 5-chloro-1-indanone were readily converted to the oxime ethers (156) by O-alkylation of the corresponding oxime.Thermolysis gave the desired product only in poor yield.Scheme 79.



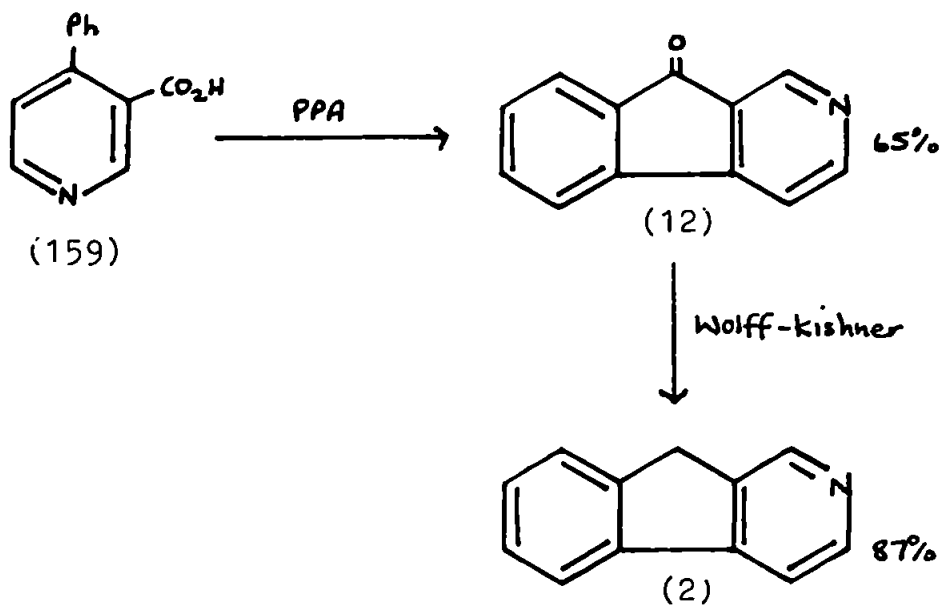
Scheme 79

The final method investigated by DuPriest [24] was based on a method developed by Abramovitch [42].Arylation of 2-fluoro-3-methylpyridine (157) with phenyllithium gave 3-methyl-2-phenylpyridine (79) which on permanganate oxidation gave the corresponding acid (158) which was cyclised with polyphosphoric acid to afford 5H-indeno[1,2-b]pyridin-5-one (8).The ketone (8) was reduced to 5H-indeno[1,2-b] pyridine (4) by treatment with excess hydrazine in diethylene glycol or by a Wolff-Kishner reduction.Scheme 80.



Scheme 80

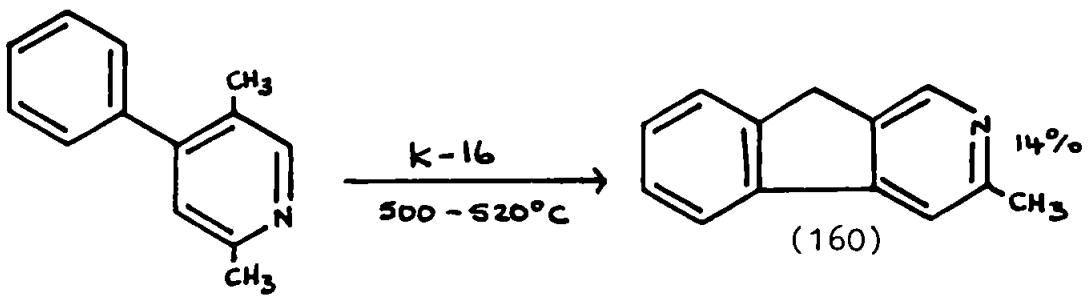
In a similar way, cyclisation of 4-phenyl-3-nicotinic acid (159) with PPA by Shiao et al [67], afforded 9H-indeno[2,1-c]-pyridine-9-one (12) which gave 9H-indeno[2,1-c]pyridine (2) by Wolff-Kishner reduction.Scheme 81.



Scheme 81

Another convenient method for the synthesis of condensed tricyclic pyridines is by intramolecular cyclisation of 4-arylpyridines.

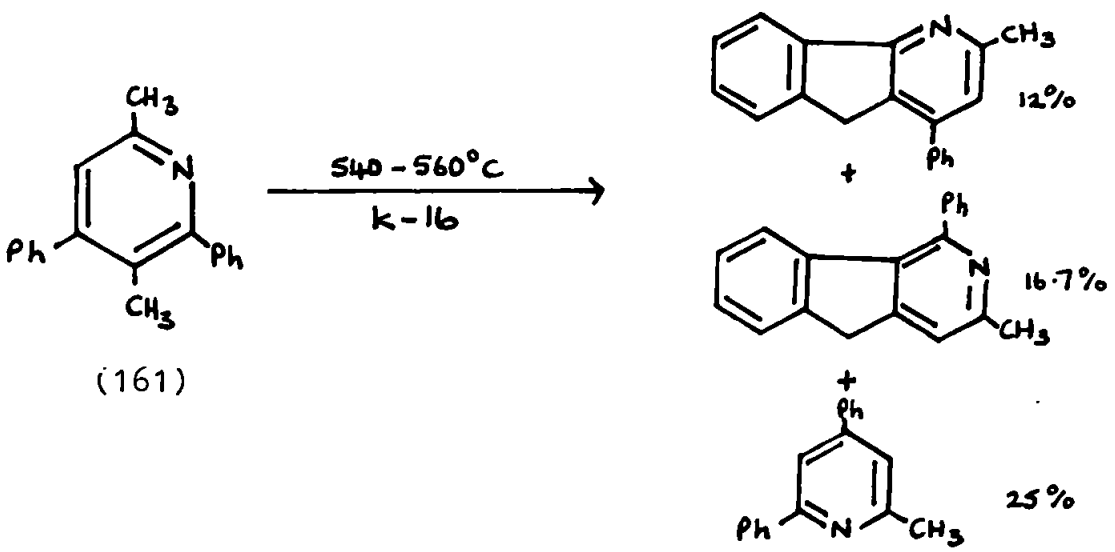
Prostakov et al[68] prepared 3-methyl-9H-indeno[2,1-c]pyridine (160) from 2,5-dimethyl-4-phenylpyridine by catalytic dehydrogenation at 500-520°C in the presence of K-16 catalyst (K-16 is a mixture of oxides of Fe,Zn and Cr). Scheme 82.



(160)

Scheme 82

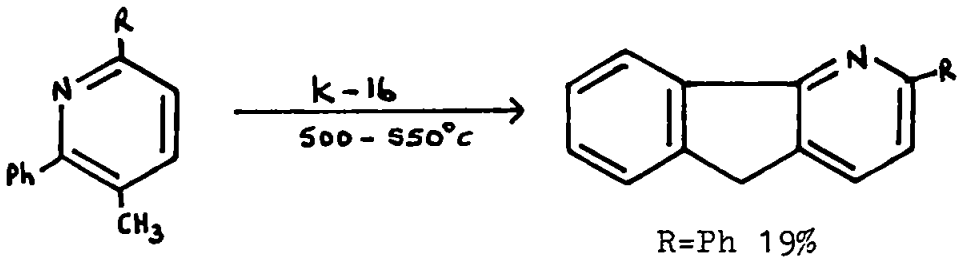
When more highly substituted pyridines were used eg., 2,5-dimethyl-4,6-diphenylpyridine (161), a complex reaction mixture was obtained from which derivatives of isomeric indenopyridines were isolated.Scheme 83



(161)

Scheme 83

Later, Prostakov[68] reported improved yields of substituted indenopyridines by dehydrocyclisation of 3-methyl-2,6-diphenylpyridine and 3-methyl-2-phenylpyridine.Scheme 84.



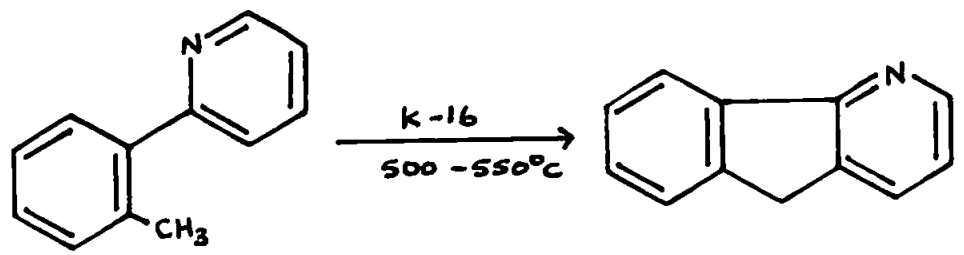
R=Ph,H

R=Ph 19%

R=H 22%

Scheme 84

Dehydrocyclisation of 2-(2'-methylphenyl)pyridine (162) gave 5H-indeno[1,2-b]pyridine (4) in 18% yield.Scheme 85.



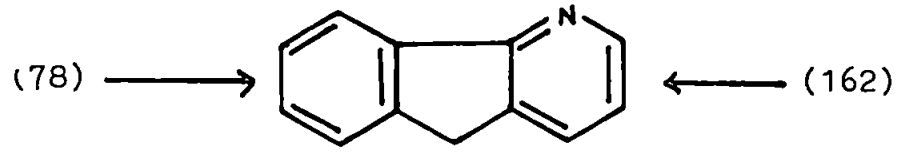
(162)

(4)

Scheme 85

Prostakov[21] also found catalytic dehydrocyclisation to be convenient for the synthesis of various substituted 5H-indeno[1,2-b]pyridines.For example, 3-methyl-2-phenylpyridine (78) , 2-(2'-methylphenyl)pyridine (162) and 3-methyl-2,6-diphenylpyridine (163) were subjected to catalytic dehydrocyclisation. The yields of (4) were almost identical regardless of whether cyclisation was realised with respect to the phenyl ring or pyridine ring,

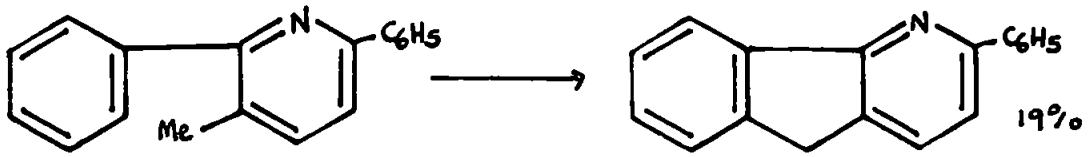
(22% (78) ; 18% (162)). Scheme 86.



(4)

Scheme 86

Similarly, catalytic dehydrocyclisation of (163) afforded 2-phenyl-5H-indeno[1,2-b]pyridine (19).Scheme 87.



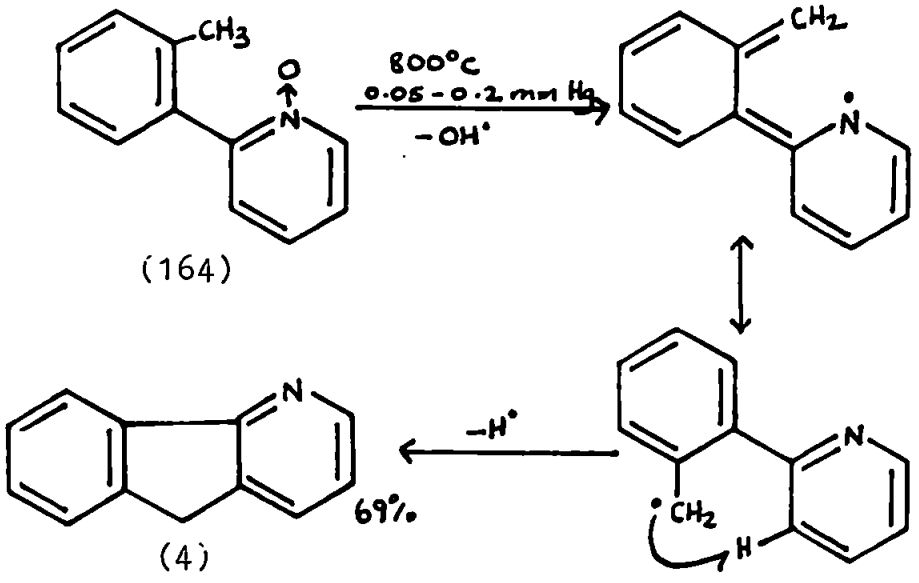
(163) (19)

Scheme 87

A different approach to the formation of the five-membered ring was reported by Igeta et al [69] and Ohsawa et al [70]. Using Flash Vacuum Pyrolysis (FVP), they decomposed substituted pyridine N-oxides,thermally, to yield a range of heterocyclic compounds.

Pyrolysis of 2(2'-methylphenyl)pyridine N-oxide(164) at 800°C produced (4) in 69% yield.

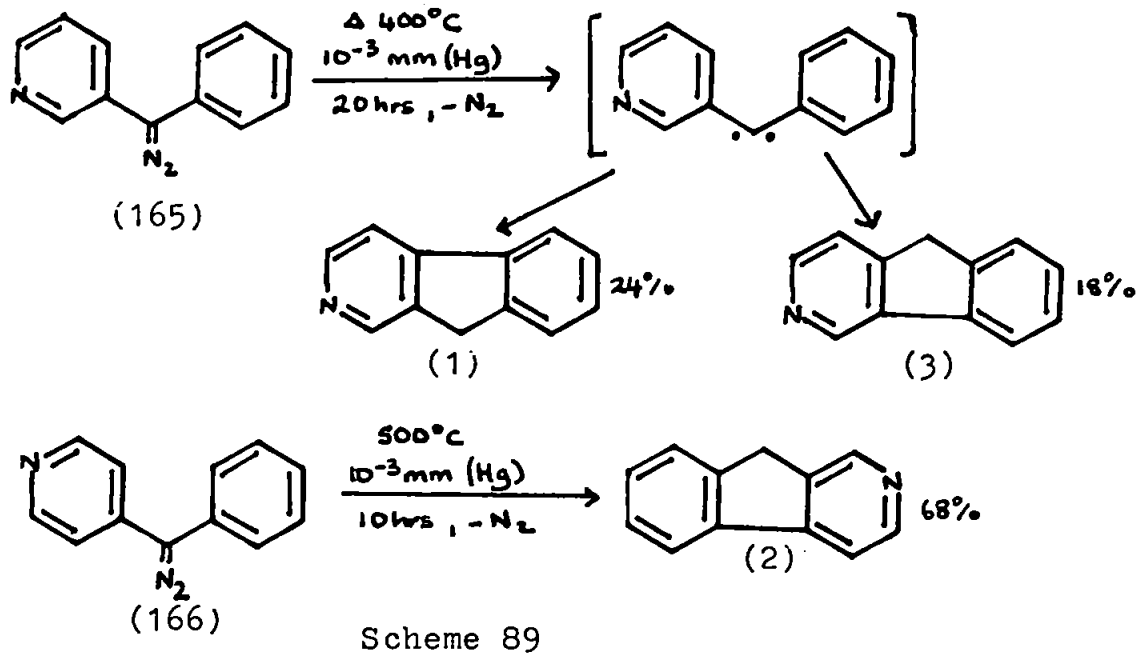
Igeta [69] suggested that the reaction proceeded via a radical process as shown in Scheme 88.



Scheme 88

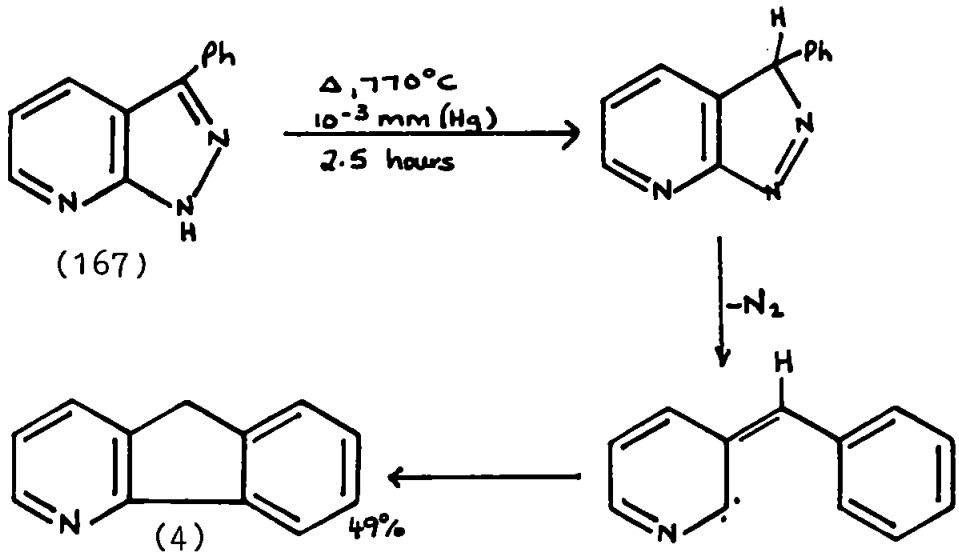
Mayor and Wentrup [71] reported the synthesis of 3 isomeric indenopyridines, which were prepared by the thermal decomposition of phenylpyridyldiazomethanes.

Thermolysis of phenyl 3-pyridyldiazomethane (165) yielded a 1:1 mixture of 9H-indeno[2,1-b]pyridine (1) and 5H-indeno[1,2-c]pyridine (3), whereas phenyl 4-pyridyl-diazomethane (166) gave 9H-indeno[2,1-c]pyridine (2) via intermediate carbenes, as shown in Scheme 89.



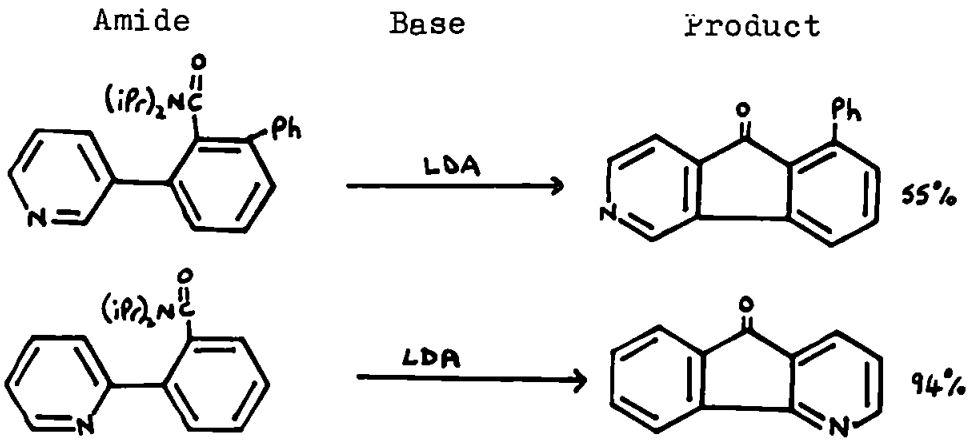
Scheme 89

Wentrup et al [72] extended this work by investigating an alternative procedure for generating the carbenes which were claimed to be intermediates in Scheme 89. Thermolysis of the indazole , 3-phenylpyrazolo[3,4-b]-pyridine (167) gave 5H-indeno[1,2-b]pyridine (4) in 49% yield.Scheme 90.



Scheme 90

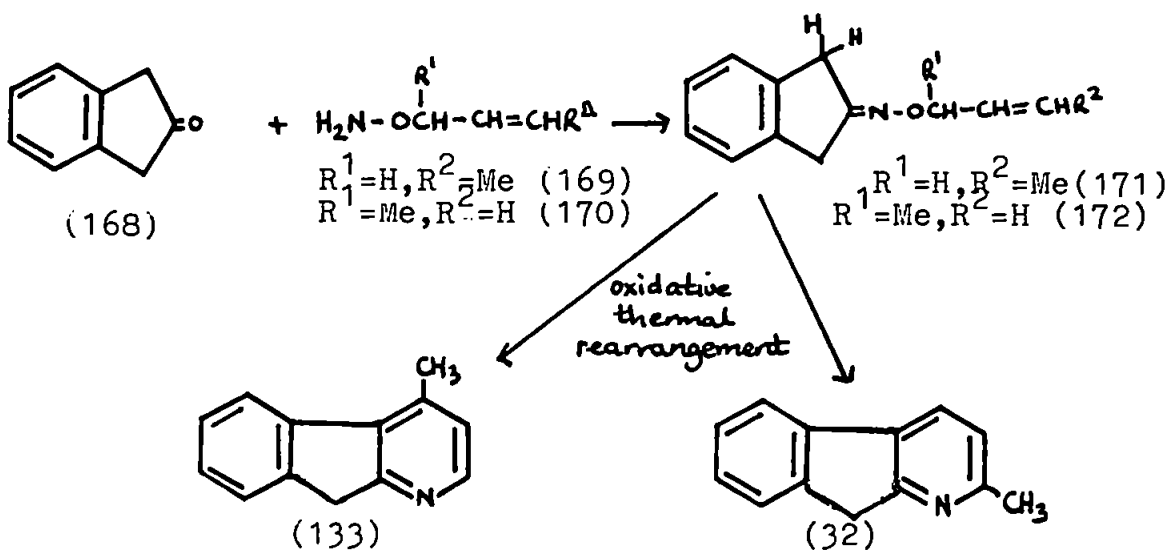
In 1991, Fu et al [73] discovered a short route to a variety of substituted and condensed fluorenones, including aza analogues by remote metalation (t-butyllithium and lithium diisopropylamide (LDA)) of m-teraryl and biaryl amides. LDA is the more effective base for the production of indenopyridines.Scheme 91.



Scheme 91

Type 2. Syntheses involving Construction of the pyridyl ring using derivatives of indane as starting material.

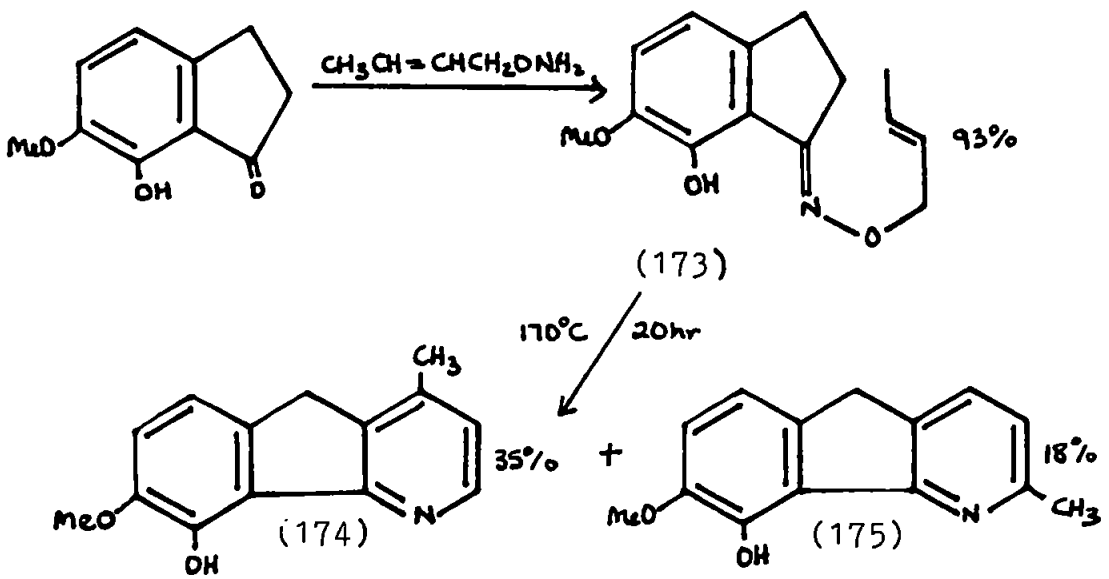
Koyama et al [74] treated 2-indanone (168) with O-crotyl- (169) or O-α-methylallyl-hydroxylamine (170) to give 2-indanone oxime O-crotyl-(171) and O-α-methylallyl ether (172) respectively in good yields. Thermolysis of each compound in a sealed tube for 48 hours furnished a mixture of two isomeric indenopyridines (133) and (32) according to Scheme 92.



Scheme 92

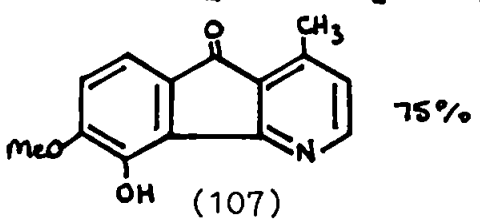
Permanganate oxidation gave the corresponding oxo-compounds.

Later, starting from 7-hydroxy-6-methoxyindanone and crotylhydroxylamine, Koyama [75] obtained the oxime (173). Thermolysis at 170°C for 2 hours produced 9-hydroxy-8-methoxy-4-methyl-5H-indeno[1,2-b]pyridine (174) and 9-hydroxy-8-methoxy-2-methyl-5H-indeno[1,2-b]pyridine (175).Scheme 93.

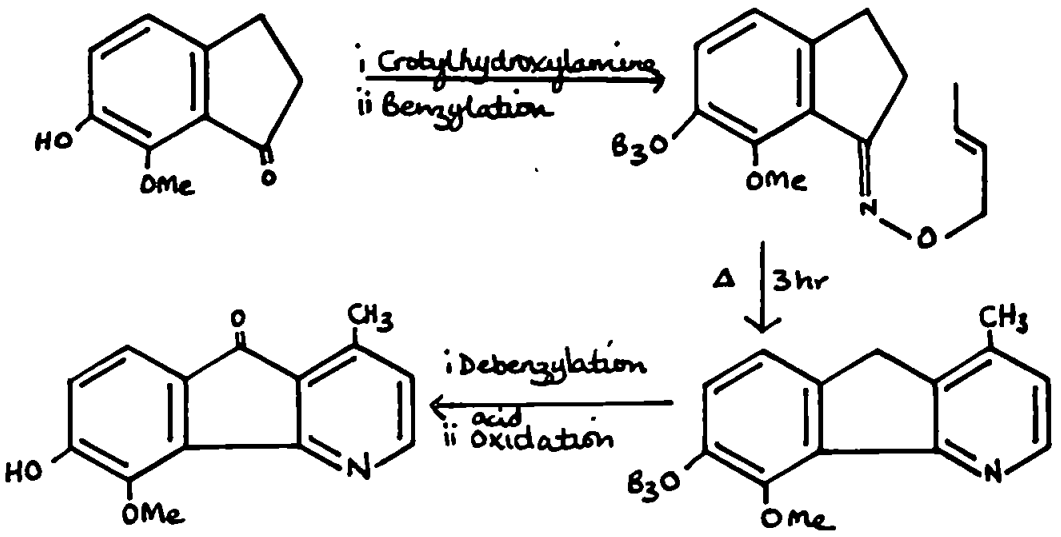


Scheme 93

Methoxymethylation of (174), followed by oxidation and demethoxymethylation with H_2SO_4/CH_3CO_2H gave 9-hydroxy-8-methoxy-4-methyl-5H-indeno[1,2-b]pyridin-5-one (107)



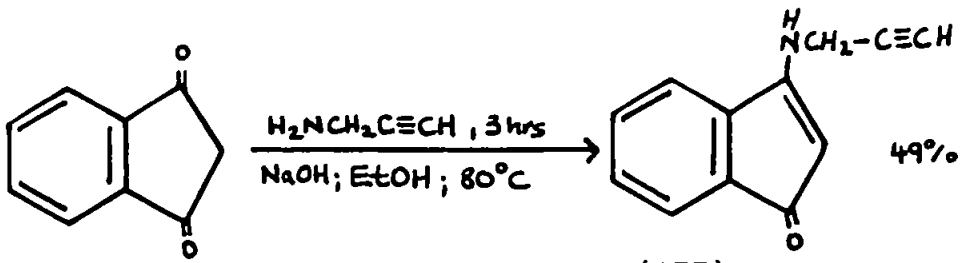
In the same manner, 8-hydroxy-9-methoxy-4-methyl-5H-indeno[1,2-b]pyridin-5-one (176) was obtained from 6-hydroxy-7-methoxyindanone, after benzylation of the hydroxyl group. Scheme 94.



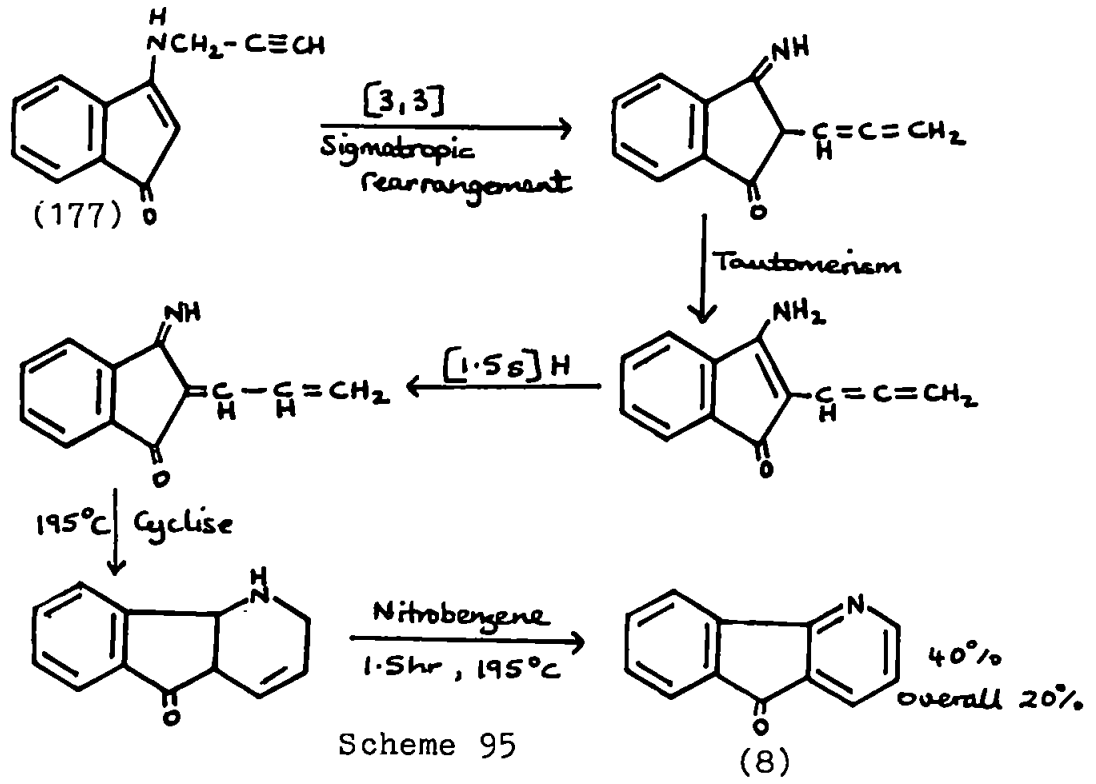
(176)

Scheme 94

Skatterbøl and Berg-Neilson[76] used 1,3-dioxoindane and 3-aminopropyne to prepare 3(2-propynlamino)inden-1-one (177) which was converted to 1,2-dihydro-5H-indeno[1,2-b]-pyridine. Dehydrogenation of the dihydro compound with nitrobenzene gave the indenopyridine (8). They suggest that conversion of propynylaminoindene to the dihydro-compound involves an Amino Claisen rearrangement followed by ring closure , as shown in Scheme 95.



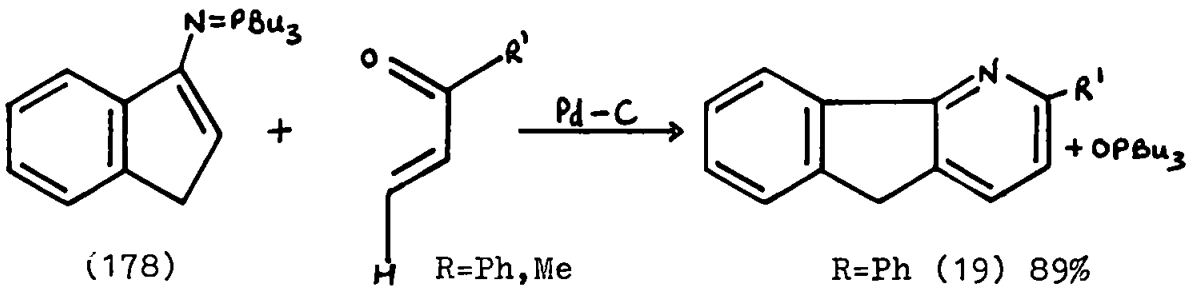
(177)



Scheme 95

(8)

Nitta et al[25] have developed a new synthesis of 5H-indeno-[1,2-b] pyridine (4) and 5H-indeno[1,2-b] pyridin-5-ones (8). Thermal reaction of tributyl(inden-3-ylimino)-phosphorane (178) with α, β -unsaturated ketones and aldehydes led to a Michael-type C-C bond formation and subsequent aza-Wittig reactions gave 5H-indeno[1,2-b] pyridine derivatives.Scheme 96.



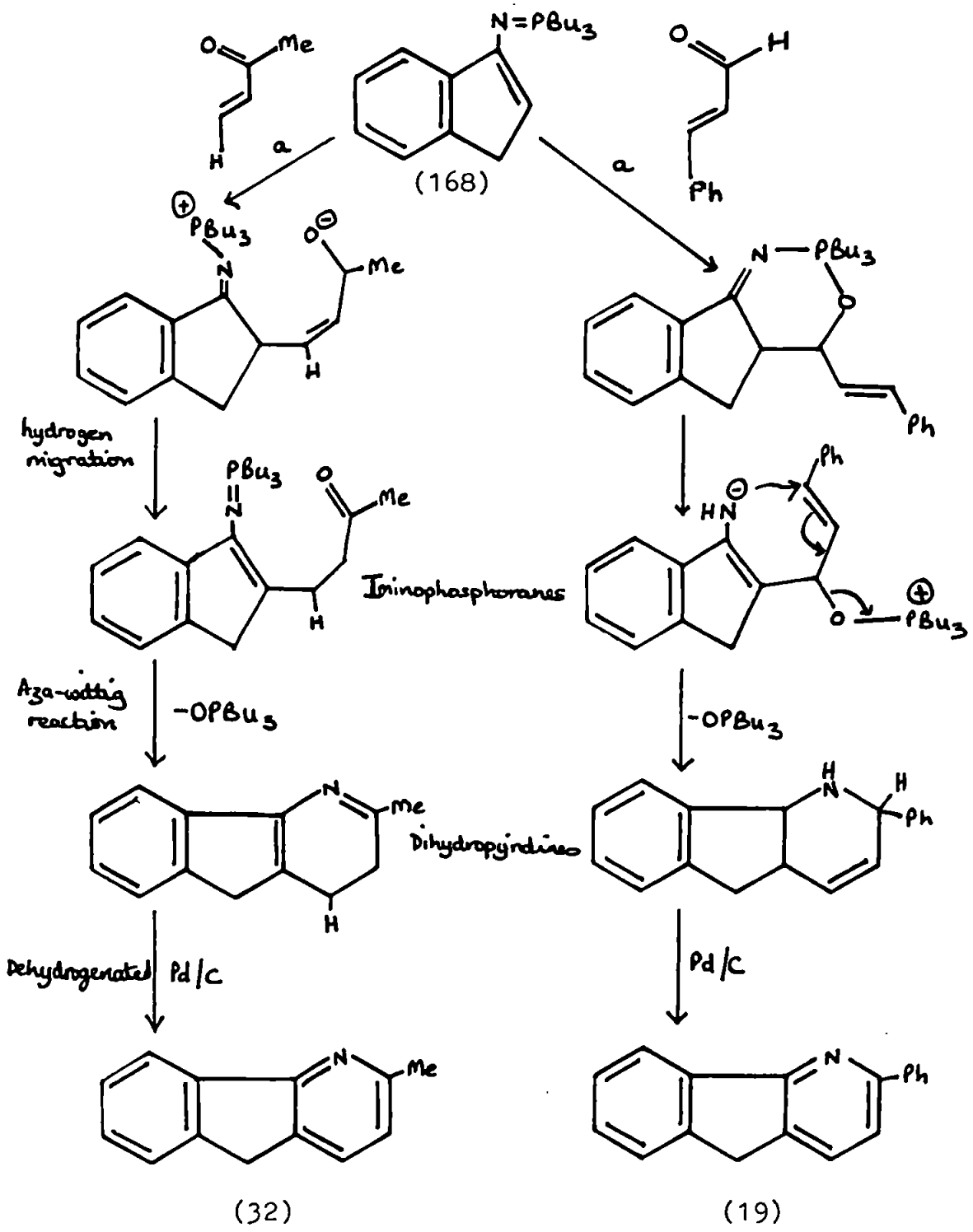
(178) R=Ph,Me

R=Ph (19) 89%

R=Me (32) 62%

Scheme 96

The pathway for the formation of 2-methyl-5H-indeno[1,2-b]-pyridine (32) and 2-phenyl-5H-indeno[1,2-b]pyridine (19) are shown in Scheme 97.

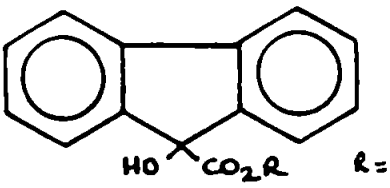


a. enamine type alkylation
(Michael addition)

Scheme 97

Chapter 7. Objective of the Research

Smith[77] in 1986, whilst attempting to make some aza analogues of morphactins (179) had been obliged to seek a high yield, low cost route to his starting material, 5H-indeno[1,2-b]pyridine (4), since the only supplier of this compound had withdrawn it from the market.

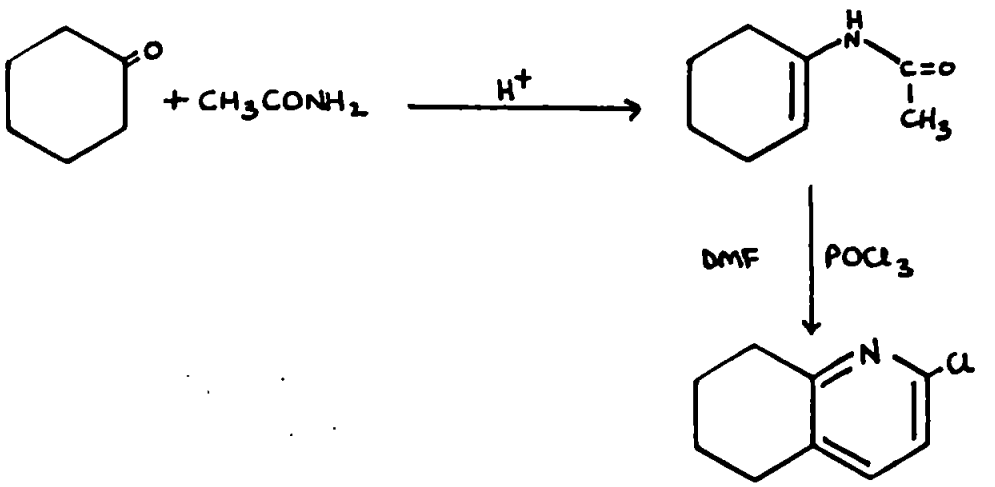


(179)

As at this time no high yield, low cost route had been developed, Smith[77] attempted two novel routes to this material (4).

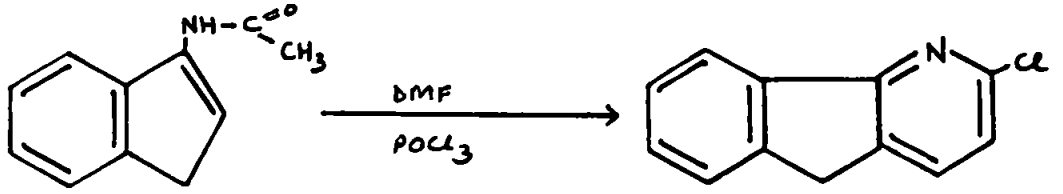
(1) The Vilsmeier-Haack formylation of enamides.

This is based on the synthesis of quinolines and fused pyridines developed by Meth-Cohn and Westwood[78]. Scheme 98.

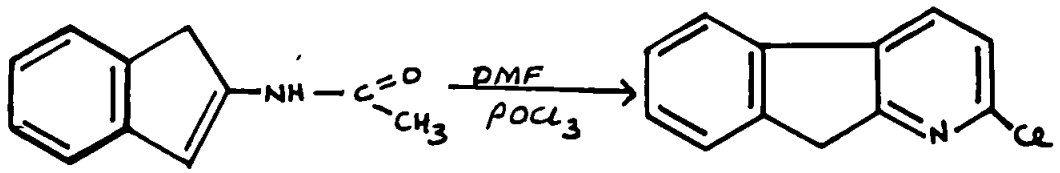


Scheme 98

Theoretically, enamides derived from 1- and 2-indanone would produce 2-chloroindeno[1,2-b]pyridine(180) and 2-chloroindeno[2,1-b]pyridine (181) respectively. Scheme 99.



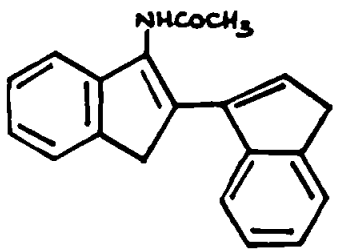
(182) (180)



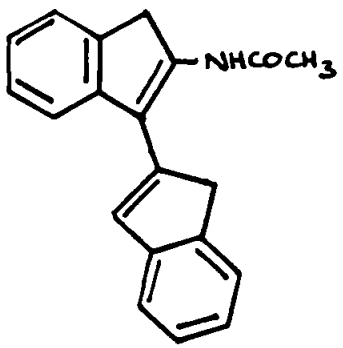
(183) (181)

Scheme 99.

Attempts by Smith[77] to prepare enamides (182 and 183) were only partially successful due to the concomitant formation of the unusual condensation products (184 and 185).



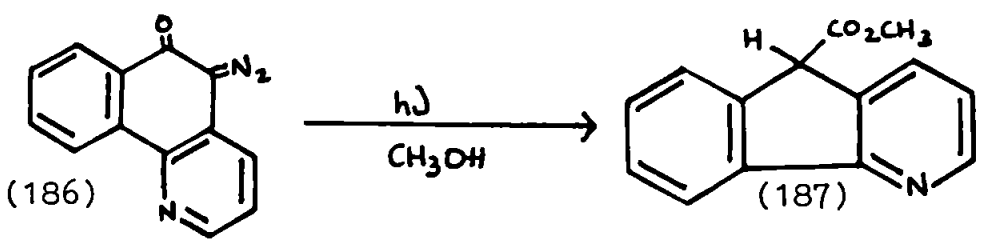
(184)



(185)

(2). The Wolff rearrangment of benzoquinoline diazoketones.

Theoretically, the Wolff rearrangement of benz[h]quinolin-5,6-diazoketone (186) in methanol should provide methyl 5H-indeno[1,2-b]pyridin-5-carboxylate (187) Scheme 100.



(186) (187)

Scheme 100

Smith[77] found , however, that the product was a dimer, but did not investigate alternative reaction conditions which might prevent dimer formation.

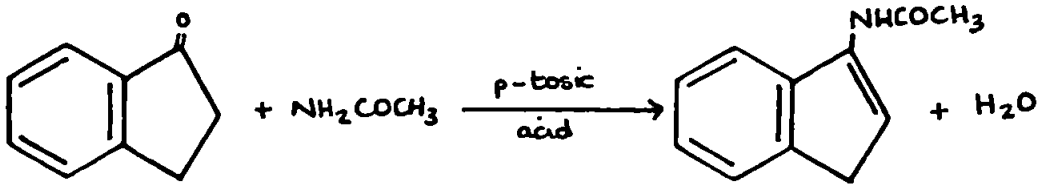
Although neither method was taken to completion, both routes had produced some interesting chemistry.

The present study commenced in 1987 with the object of exploring and developing the routes to 5H-indeno[1,2-b]-pyridine (4) chosen by Smith[77] and investigating other general routes to these compounds with the view to increasing the knowledge of this fairly uncommon class of compound.

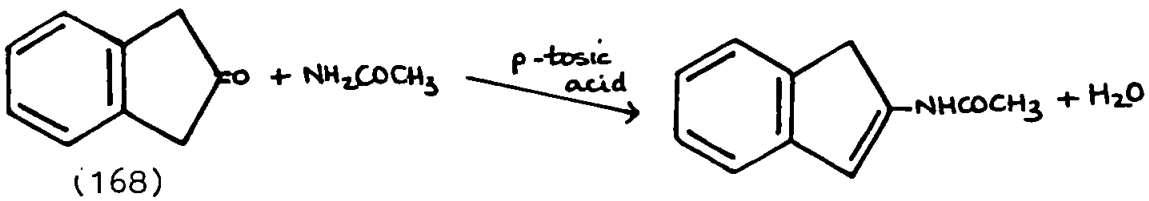
Chapter 8. Synthesis of Indenopyridines by the Vilsmeier-Haack formylation of enamidoindenes.

As previously mentioned, Smith[77] (1987) attempted to prepare indenopyridines by the Vilsmeier-Haack formylation of enamidoindenes.Scheme 96.

Following the method of Ben-Ishai and Zehavi[79] for the preparation of 1-acetamidocyclohexene, Smith[77] attempted to prepare 1- and 2-acetamidoindene using the condensation of 1- and 2-indanone and acetamide in the presence of the catalyst toluene-4-sulphonic acid (p-tosic acid).Scheme 101.



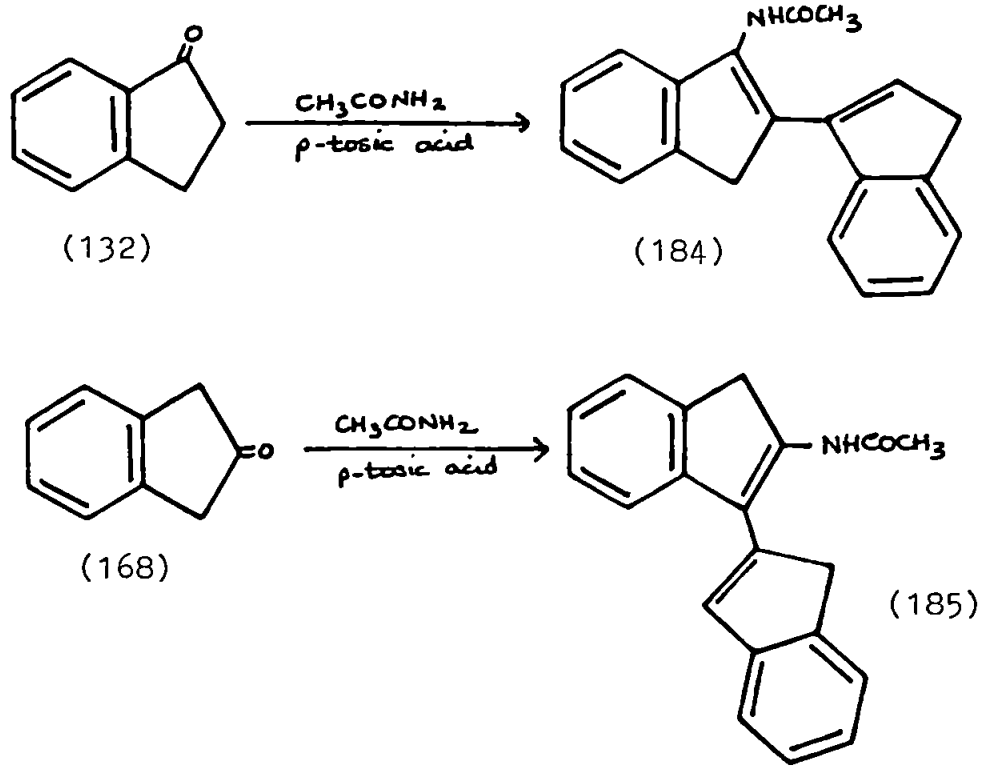
(132) (182)



(168) (183)

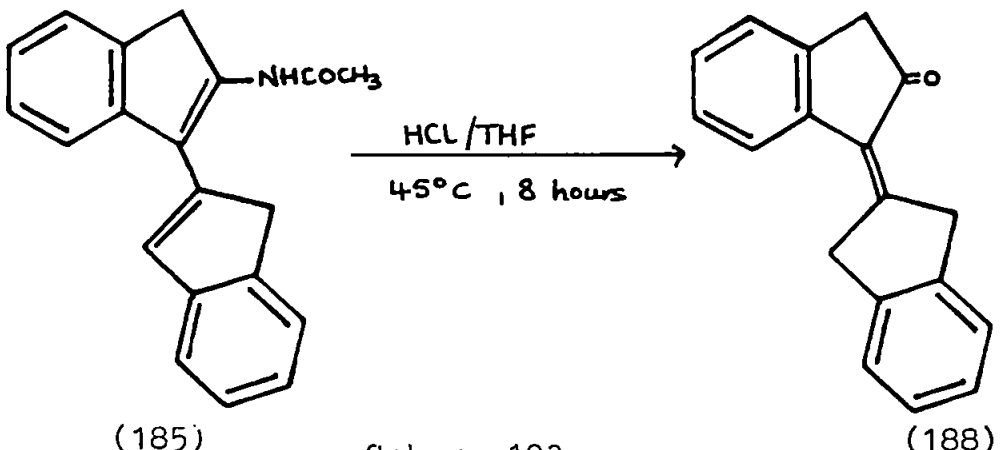
Scheme 101

However, the expected enamides were not obtained. Instead, unexpected di-condensation products (184, 185) were obtained.Scheme 102.



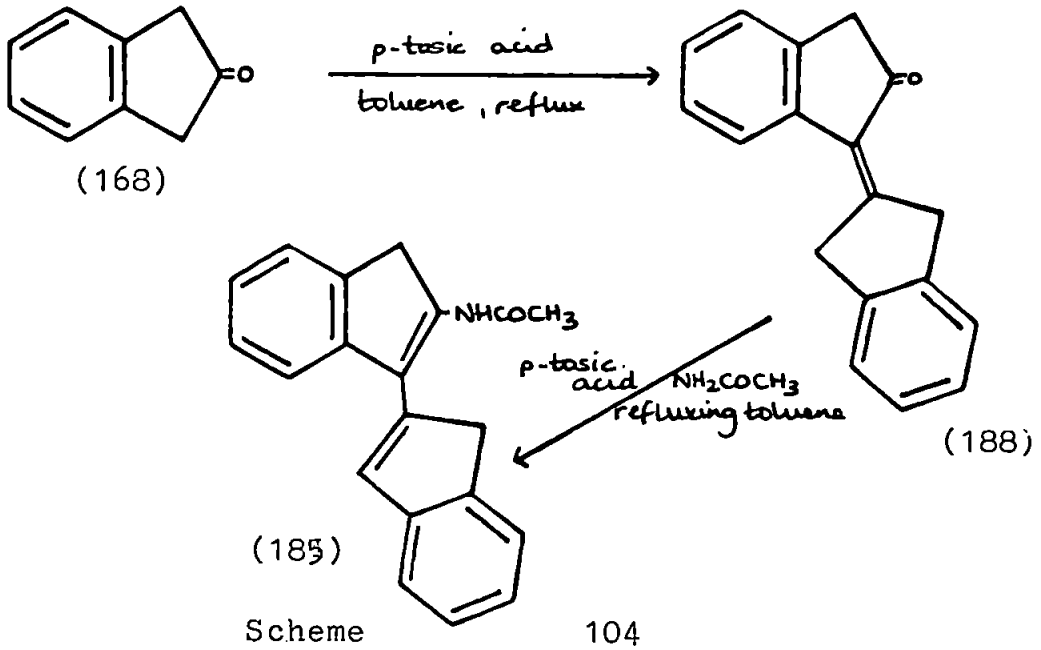
Scheme 102

Smith[77] confirmed the structure of 2-acetamido-1(2'-indenyl)-indene (185) by hydrolysis of the enamide function. Treatment of (185) with hydrochloric acid in tetrahydrofuran gave the corresponding ketone- 1(2'-indanylidene)-indan-2-one (188). Scheme 103.



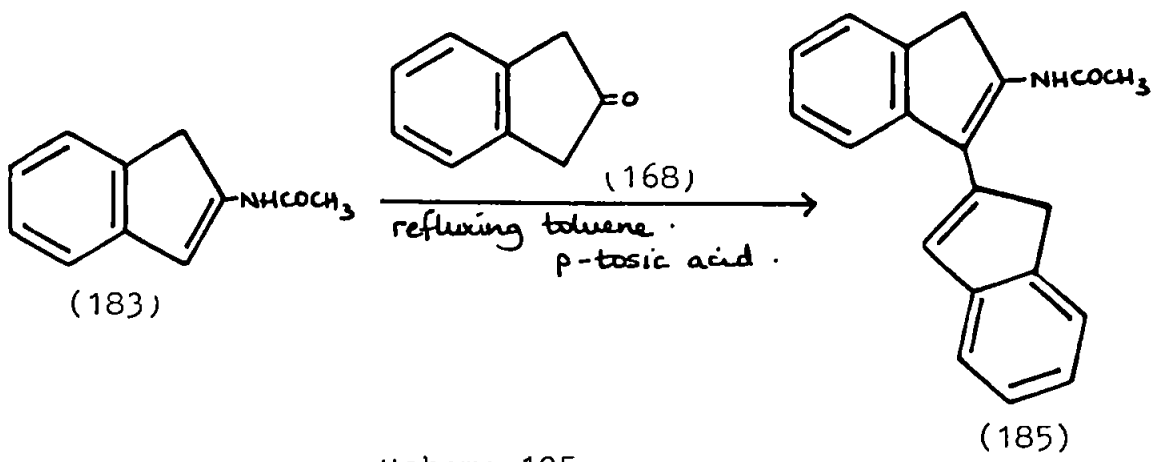
Scheme 103

Smith[77] proposed that the acetamidoindenylindenes might therefore be formed by self-condensation of the indanone, followed by enamide formation, as shown for the 2-compound. Scheme 104.



Scheme 104

Alternatively, the first step in the reaction might be enamide formation followed by the enamide acting as a C-nucleophile towards the unreacted ketone, as indicated for the 2-compound in Scheme 105.



Scheme 105

Of the proposed mechanisms, Smith[77] thought that the latter, Scheme 105, was the most likely.

Smith[77] supported this mechanism by reacting 2-acetamidoindene (183) with 2-indanone (168) in refluxing toluene containing p-tosic acid. The expected di-condensation product (185) was obtained in poor yield (33%).

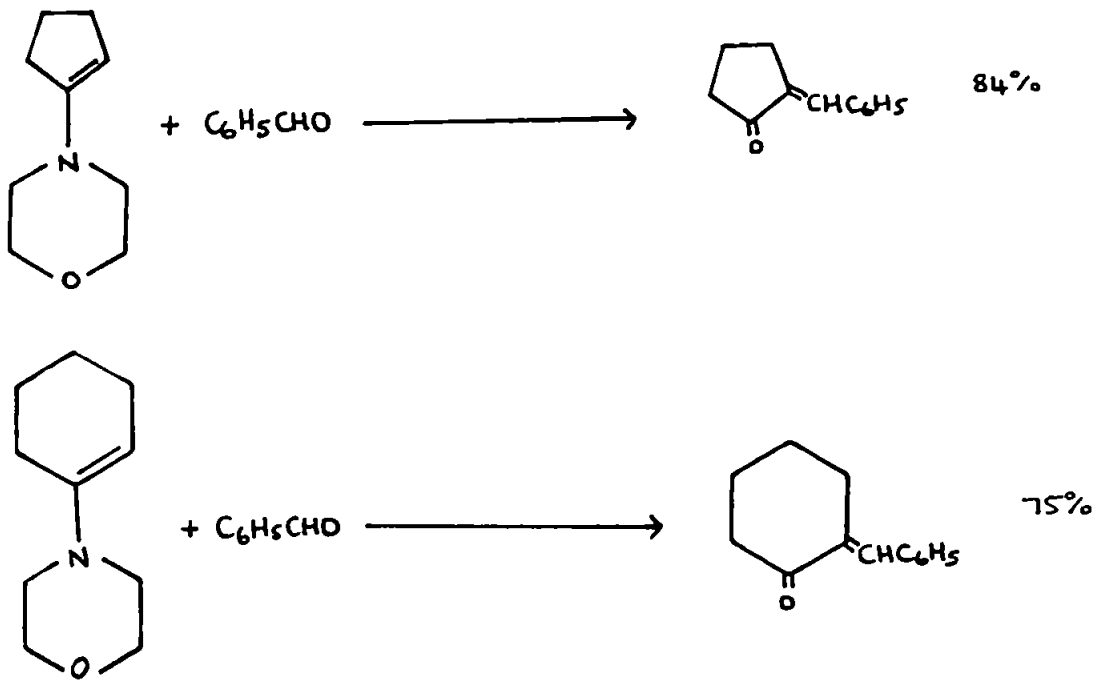
Smith[77], however, did not investigate the conversion of 1(2'-indanylidene)indan-2-one (188) to 2-acetamido-1(2'-indenyl)indene (185). Scheme 104.

The conclusions Smith[77] drew from these experiments were therefore based only on partial evidence.

One major objection to this postulated pathway is that enamides are expected to be considerably weaker C-nucleophiles than enamines[80] due to the presence of the carbonyl group adjacent to the nitrogen atom.

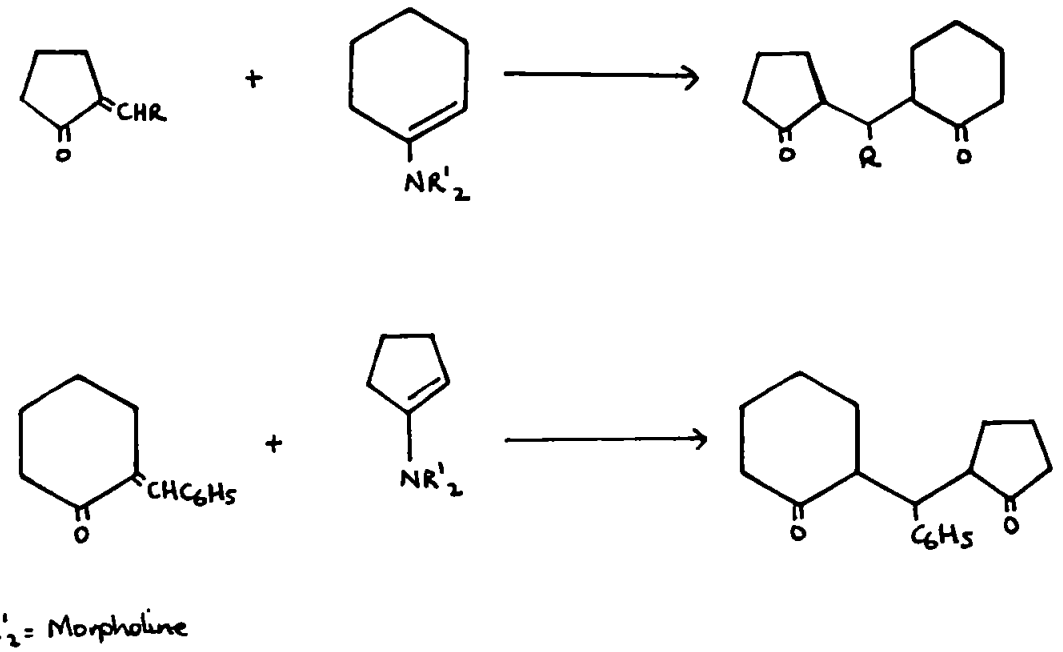
Infact, Lenz[81] states that enamides may be regarded as deactivated enamines.

Although enamines are known to react with aldehydes and ketones,[82] enamides would be expected to react even less readily. Birkofer et al[83] have found that enamines do react however, with aldehydes to give alkylidene or arylidene ketones. Scheme 106.



Scheme 106

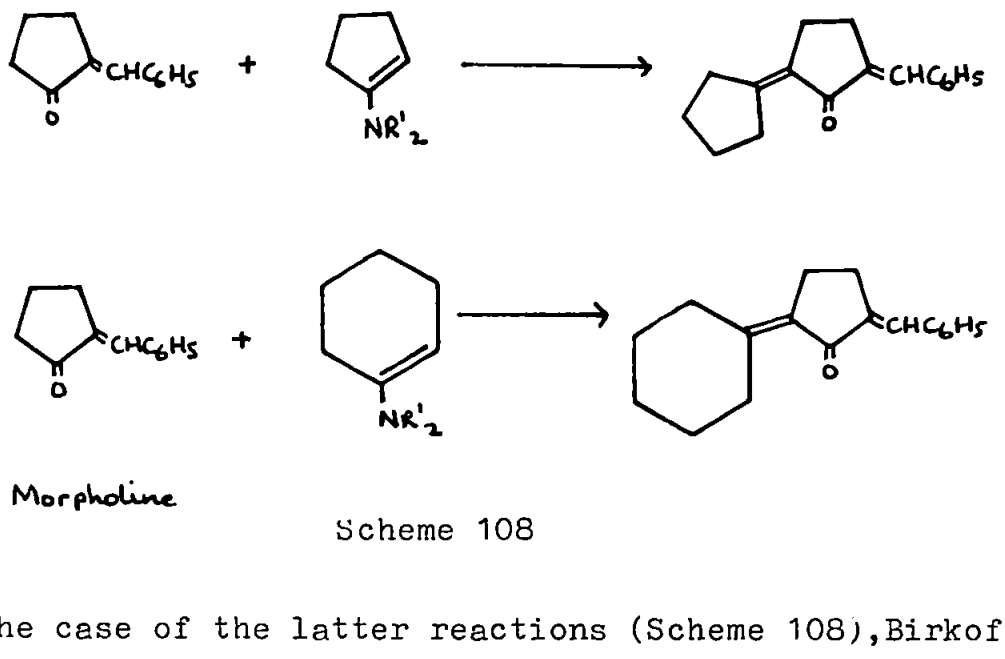
Birkofer et al[83], also found that α-alkylidene ketones reacted with N-(Δ'-cyclohexenyl)- or N-(Δ'-cyclopentyl)-morpholine to give 1,1-disubstituted alkanes. Scheme 107.



R'_2 = Morpholine

Scheme 107

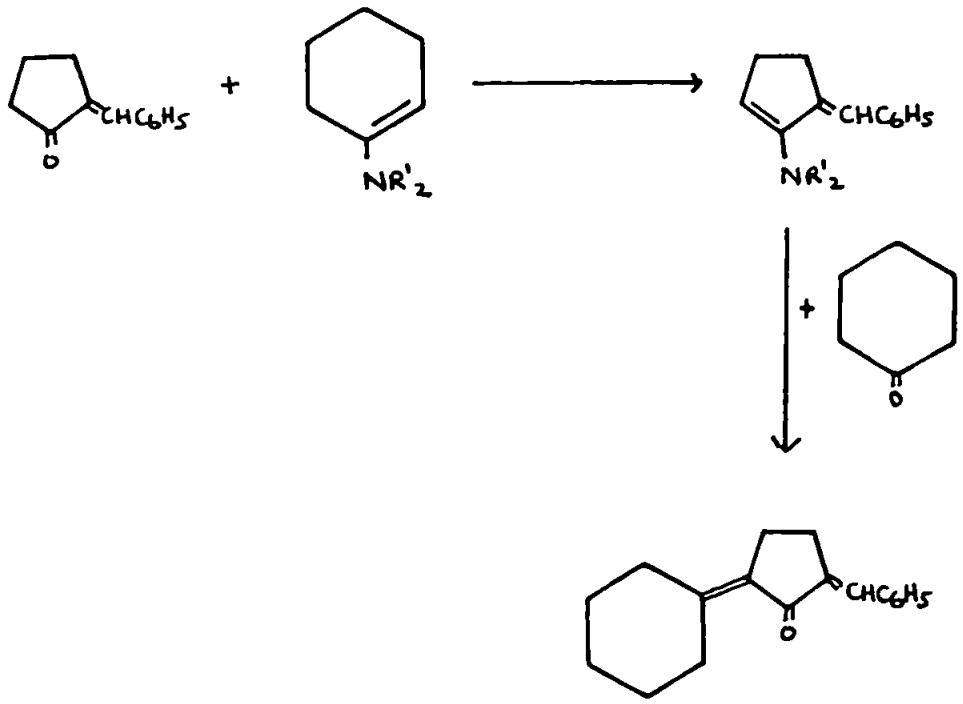
Arylidene derivatives of cyclopentanone were found to give di-condensation products. Scheme 108.



R'_2 = Morpholine

Scheme 108

In the case of the latter reactions (Scheme 108), Birkofer et al[83] claim that enamine exchange occurred as shown in Scheme 109, the unsaturated enamine which results is then claimed to act as a C-nucleophile towards cyclopentanone.



Scheme 109

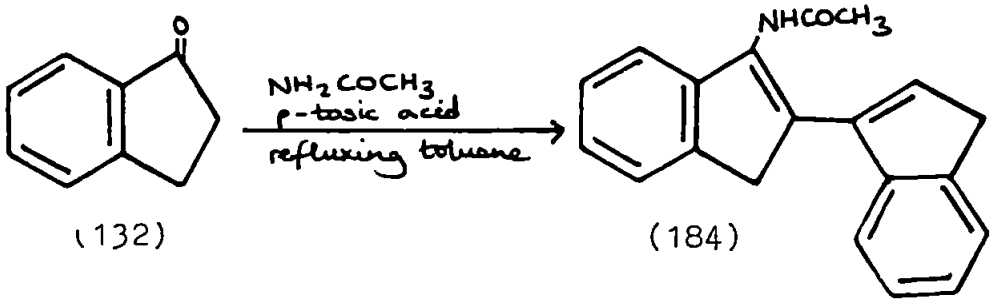
The reactions are comparable to those postulated for the formation of the enamidoindenylidenes, as indicated in Scheme 109.

In contrast to the results obtained from reacting acetamide with 2-indanone in the presence of tosic acid, Smith[77] found that omission of the tosic acid led to the successful production of 2-acetamidoindene (183) in 20% yield. However, no 1-acetamidoindene (182) could be made.

As Smith[77] was unable to determine the course of reaction by which these di-condensation products were produced, it was decided to commence the project by carrying out a more detailed investigation into the production of the di-condensation enamides in the hope that conditions might be found for a high yield synthesis of the required mono condensation products.

Some of the work of Smith[77] was therefore repeated.

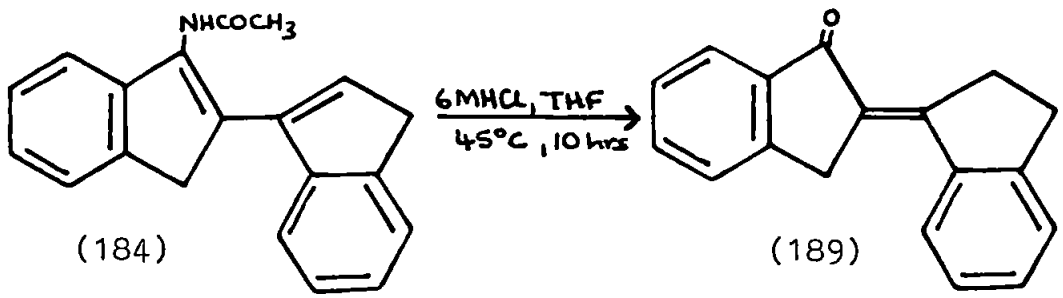
When 1-indanone (132) was reacted with acetamide in refluxing toluene, in the presence of p-tosic acid, the expected dimer, 1-acetamido-2(1'-indenyl)indene (184) was obtained in 44% yield. Scheme 110.



(132) (184)

Scheme 110

The identity of the dimer was confirmed by hydrolysis of (184) with 6M HCl in tetrahydrofuran at 45°C for 10 hours. The enamide function was hydrolysed giving the corresponding ketone - 2(1'-indanylidene)indan-1-one (189) in 38% yield. Scheme 111.



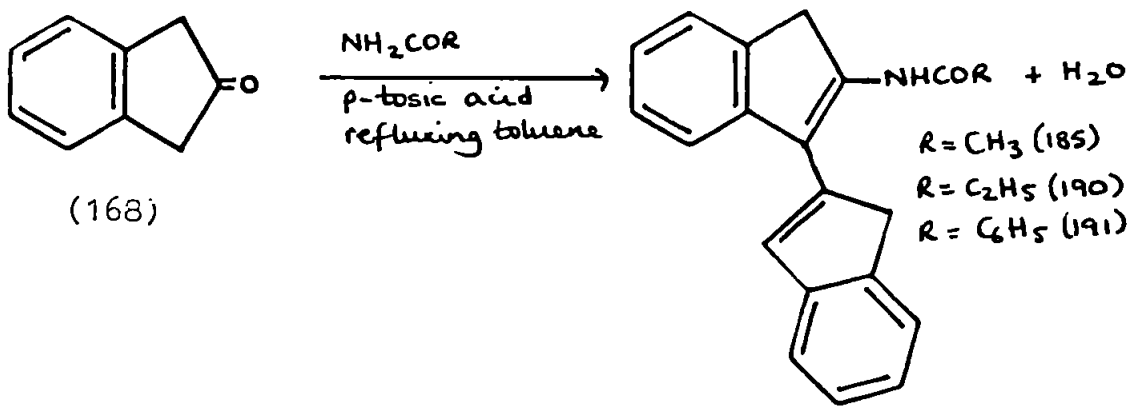
(184) (189)

Scheme 111

An attempt to extend the synthesis of the 1-enamidoindenyl-indenes using different amides, namely propionamide, benzamide and cinnamamide was undertaken. All of the aforementioned amides failed to react with 1-indanone (132) in the presence of acid catalyst.

In each case the starting amide was recovered, together with a small amount of 1-indanone (132) and an unknown product with a relative molecular mass of 342, to which reference will be made later in the chapter.

The reaction of 2-indanone (168) with acetamide in the presence of p-tosic acid, in refluxing toluene, produced 2-acetamido-1(2'-indenyl)indene (185) in 76% yield. Scheme 112.

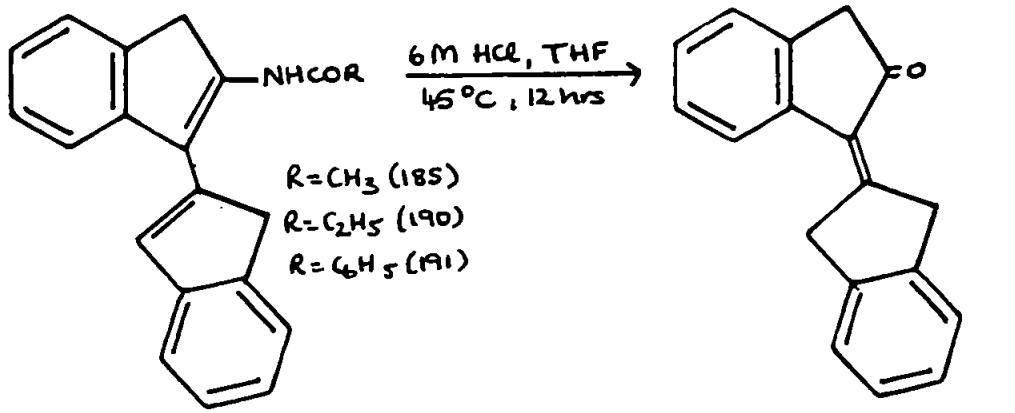


(168)

Scheme 112

Under similar conditions, 2-propionamido-1(2'-indenyl)-indene (190) and 2-benzamido-1(2'-indenyl)indene (191) were formed in 23 and 48% yields respectively. Scheme 112. Cinnamamide ,however, failed to react. In this case starting material was recovered, together with a product of unknown structure, which had a relative molecular mass of 356. (Appendix 1.12)

Again, the identity of the 2-enamidoindenylindenes were confirmed by hydrolysis. When compounds (185), (190) and (191) were treated with 6M HCl in tetrahydrofuran at 45°C for 12 hours, the enamide function was hydrolysed to give the corresponding ketone- 1(2'-indanylidene)indan-2-one (188). Scheme 113.

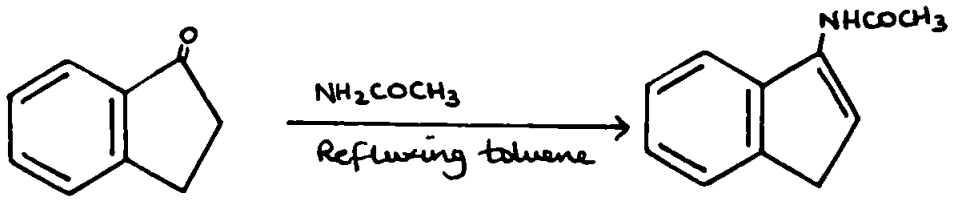


(188)

Scheme 113

Attempts were then made to prepare 1-acetamidoindene (182) following the method of Smith[77] by heating acetamide with 1-indanone (132) in refluxing toluene, in the absence of the catalyst.Scheme 114.

Although according to Smith[77], this reaction did not succeed, in this case a small amount of product was obtained, which could not be purified satisfactorly by recrystallisation. The product possibly contained the enamide, as evidenced by mass spectrometry (appendix 1.2)

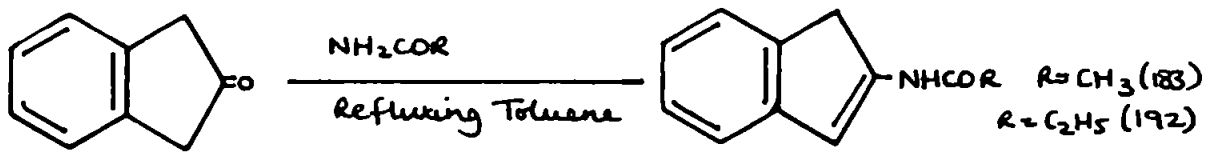


(132) (182)

Scheme 114

Under similar conditions, the amides propionamide, benzamide and cinnamamide failed to react with 1-indanone (132).

The reaction between 2-indanone (168) and acetamide in refluxing toluene, in the absence of the catalyst, did work however, to give 2-acetamidoindene (183) in moderate yield (46%).Scheme 115.

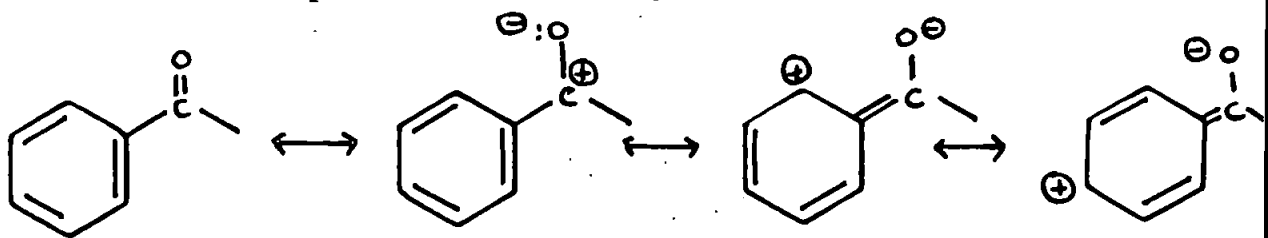


(168)

Scheme 115

Under similar conditions, 2-propionamidoindene (192) was prepared in 34% yield. Benzamide and cinnamamide, however, failed to react with 2-indanone (168).

From these results, it appears that attack by the amides is more facile at the 2-position, than the 1-position, to form the respective enamides.
This may be due to electronic effects; it is possible that nucleophilic attack does not occur because the charge on the carbonyl group of 1-indanone (132) is delocalised throughout the benzene ring, making the carbonyl carbon much less electrophilic.Scheme 116.



Scheme 116

When the carbonyl group is in the 2- position, charge delocalisation cannot occur because the carbonyl group is no longer conjugated with the benzene ring.

It would therefore be expected that 2-indanone (168) would be more reactive than 1-indanone (132), as confirmed in the afore-mentioned experiments.

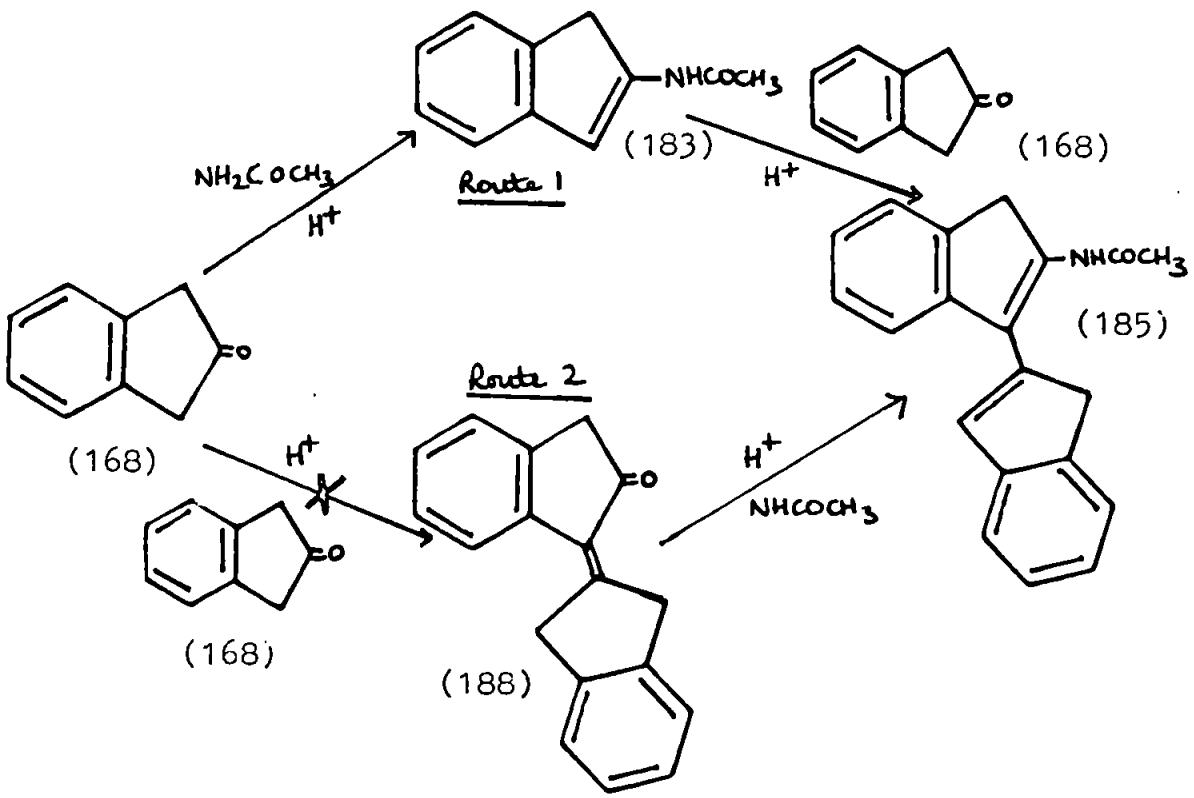
The results obtained on the reaction of 1- and 2-indanone with the various amides, both in the absence and presence of the acid catalyst , toluene-4-sulphonic acid , are summarised in Table 2 , page 89.

As indicated in Schemes 104 and 105, there are two alternative pathways by which the di-condenation enamides may be formed.

Route 1. By the enamidoindene acting as a C-nucleophile towards unreacted indanone, or

Route 2. By amide attack of the self-condensation product of indanone.

Both routes are shown below, for 2-indanone (168) and acetamide ,in Scheme 117.



Scheme 117

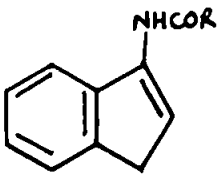
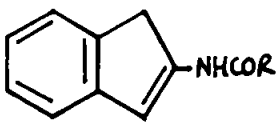
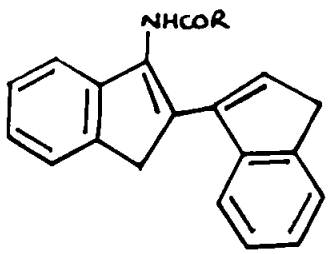
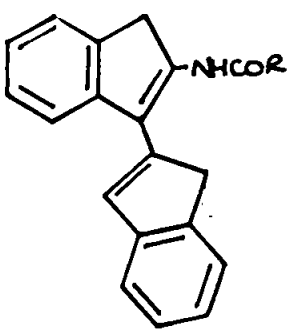
	Product \ -R	$-CH_3$	$-C_2H_5$	$-C_6H_5$	$-CH=CHC_6H_5$
WITHOUT ACID CATALYST		?	×	×	×
		46%	34%	×	×
WITH ACID CATALYST		44%	×	×	×
		76%	23%	48%	×

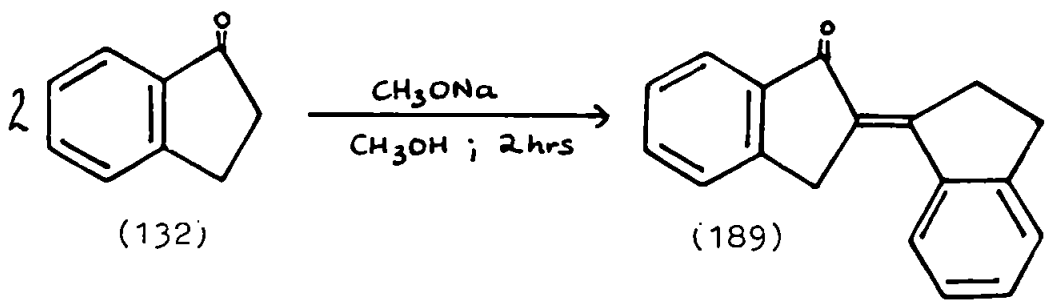
Table 2 . Summary of the reactions between amides and indanones to form enamidoindenes and enamidoindenylidenes.(% yields given.)

The feasibility of Route 2 could be examined by reacting (188) and (189) with acetamide in the presence of p-tosic acid.

The dimeric ketones - 1(2'-indanylidene)indan-2-one (188) and the corresponding isomer, 2(1'-indanylidene)indan-1-one (189) required could not be obtained commercially and had to be synthesised.

It is known that 1-indanone (132) can undergo acid-catalysed self-condensation (Kipping[84], Williams[85], Metz[86]) to form 2(1'-indanylidene)indan-1-one (189). As shown by Bell and Spanswick[87] and Metz[86] (189) may also be obtained by self-condensation under alkaline catalysis.

Using the method of Bell and Spanswick[87], the ketone (189) was prepared in 64% yield. Scheme 118.

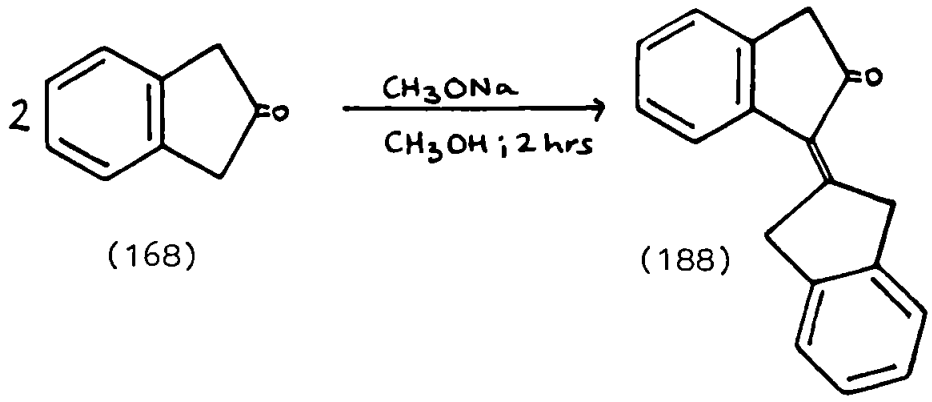


(132) (189)

Scheme 118

2-Indanone (168) can also undergo self-condensation to form 1(2'-indanylidene)indan-2-one[88] (188), apparantly, only under basic conditions , as no reference is made in the literature for the preparation of (188) under acidic conditions.

Therefore, using the method of Treibs and Schroth[68] ,(188) was obtained in 75% yield.Scheme 119.

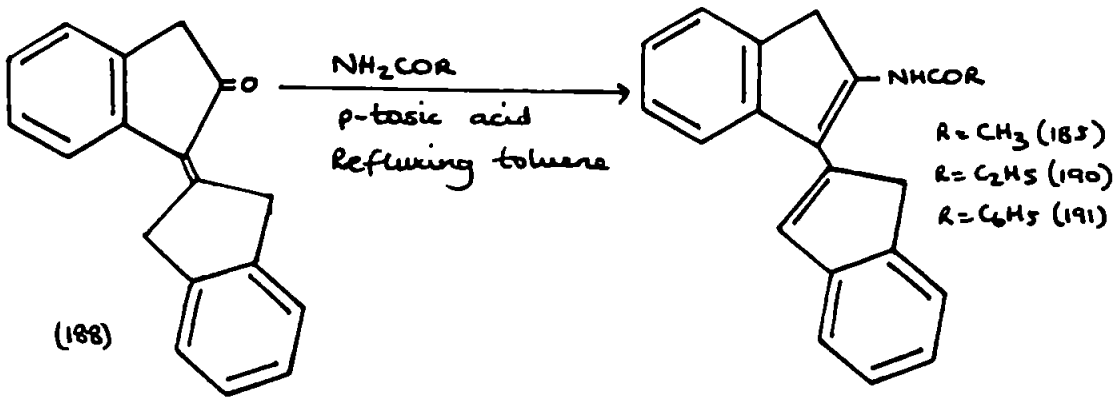


(168) (188)

Scheme 119

Although, 2-indanone (168) is not known to undergo self-condensation under acidic conditions, the possibility was examined by heating 2-indanone (168) with p-tosic acid in refluxing toluene for 2 days.
Starting materal was recovered in 65% yield, together with a product of unknown structure, which had a relative molecular mass of 360, as shown by mass spectrometry. (appendix 1.13).

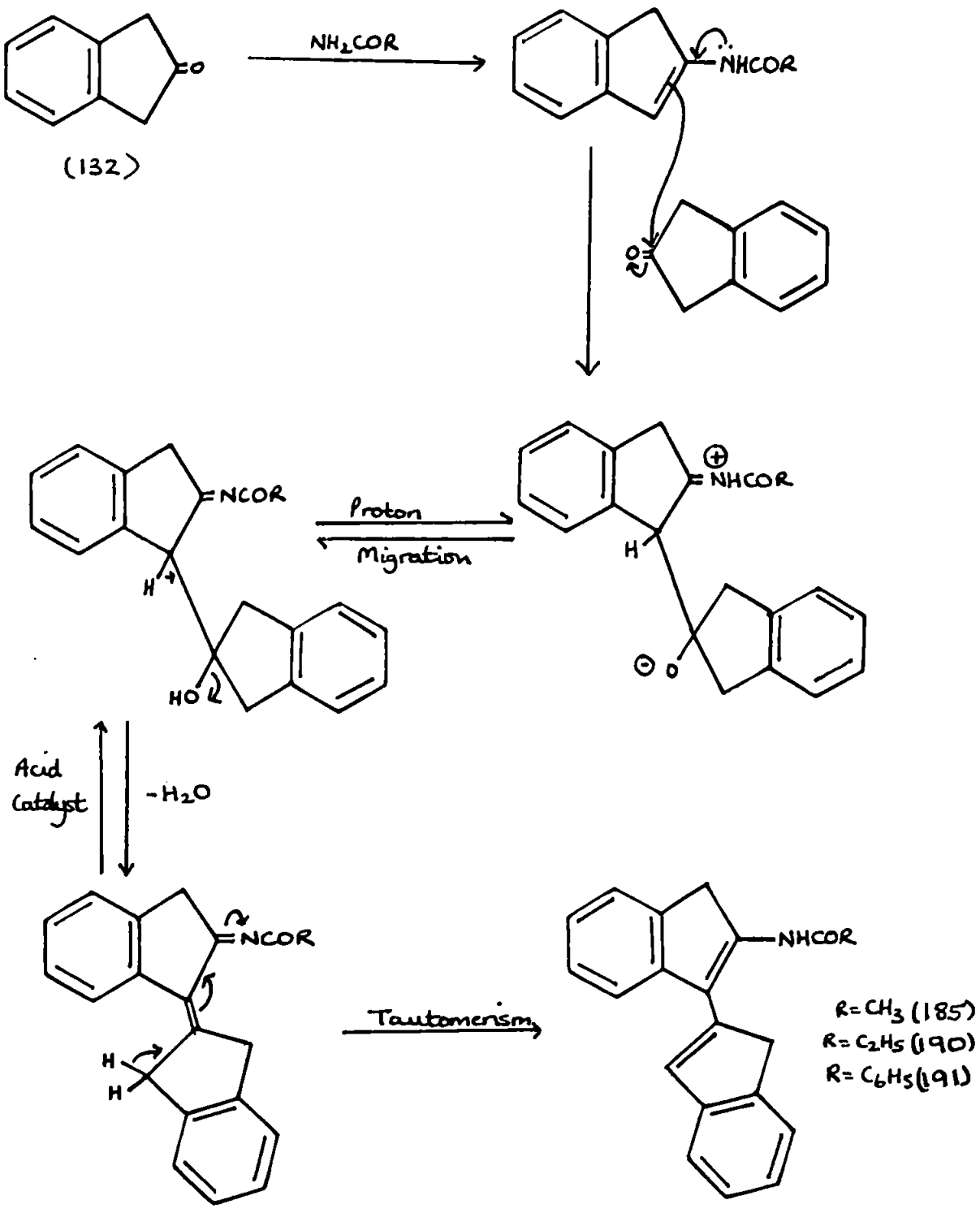
Although, for 2-indanone (168), the dimeric enamide (185) was prepared in 39% yield by reacting the dimeric ketone (188) with acetamide, under acidic conditions, since 1(2'-indanylidene)indan-2-one (188) cannot be formed under acidic conditions, it is reasonable to assume that the postulated Route 2 is incorrect. Scheme 120.



Scheme 120

The alternative route postulated (Route 1) seems therefore, more likely.The possible mechanism of formation of the dimer enamides via Route 1 is shown in Scheme 121.

Smith[77] obtained support for Route 1 by heating 2-acetamidoindene (183) with 2-indanone (168) in refluxing toluene containing p-tosic acid, to obtain the di-condensation enamide (185)in 33% yield.Scheme 105.
To confirm this finding, the above experiment was repeated. The enamide (185) was obtained in 76% yield.This finding was extended to 2-propionamide (192), where 2-propionamido-1(2'-indenyl)indene (190) was obtained in 68% yield.
The mechanism of formation of (185) and (190) maybe as shown in Scheme 121.


NH2COR
NHCOR
(132)
NCOR
Proton
Migration
NHCOR
Acid
Catalyst
-H2O
NCOR
Tautomerism
NHCOR
R=CH3 (185)
R=C2H5 (190)
R=C6H5 (191)

Scheme 121

Control experiments were carried out in order to identify the reaction route.

2-Indanone (168) and propionamide were heated together in refluxing toluene, in the presence of toluene-4-sulphonic acid. Samples were taken every ½ hour and examined by T.L.C.

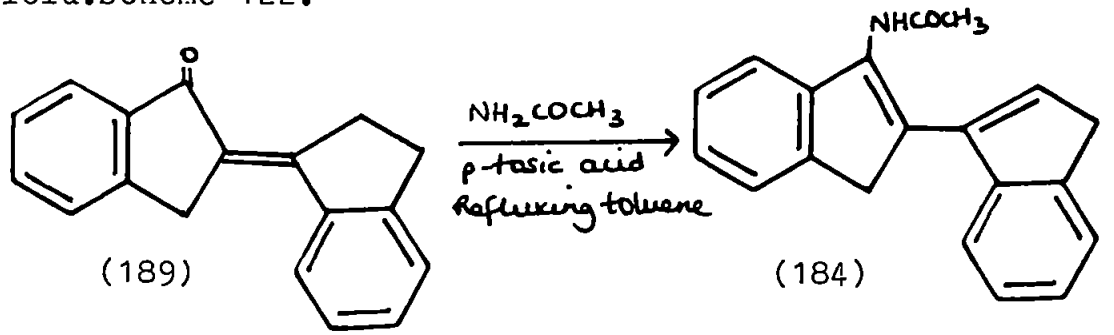
As expected, the results of this experiment suggests that the reaction proceeds via Route 1. T L C examination with authentic samples indicated that 2-propionamidoindene (192) was formed during the reaction.

On completion 2-propionamido-1(2'-indenyl)indene (190) was obtained in moderate yields.

In contrast to the 2-compound, 1-indanone (132) can undergo self-condensation under acidic conditions to form 2(1'-indanylidene)indan-1-one (189).

Therefore, the dimer - 1-acetamido-2(1'-indenyl)indene (184) may arise by the reaction of acetamide with the dimer ketone (189) - Route 2.

This was confirmed experimentally.When (189) was reacted with acetamide, in the presence of acid catalyst, 1-acetamido-2(1'-indenyl)indene (184) was obtained in 43% yield.Scheme 122.



(189) (184)

Scheme 122

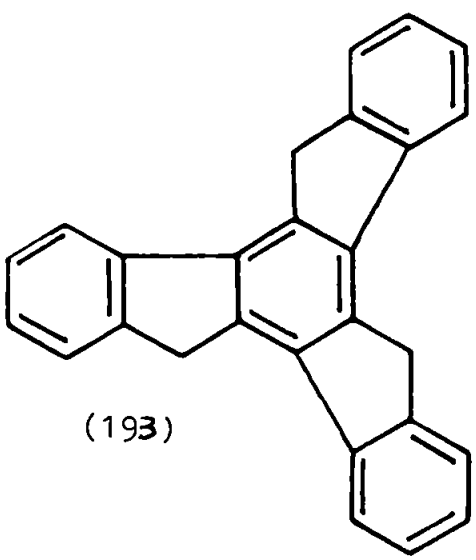
Alternatively, (184) may be obtained by 1-acetamidoindene (182) acting as a C-nucleophile towards 1-indanone (132), an addition followed by dehydration (Route 1).
This route could not be confirmed, as pure 1-acetamidoindene (182) could not be obtained.

Which route the reaction follows , for 1-indanone (132), therefore is not known.

High Molecular Weight Compounds.

The compound formed under acidic conditions, when 1-indanone (132) was heated with the amides - propionamide, benzamide and cinnamamide, in refluxing toluene, in the presence of p-tosic acid, was found to have a molecular weight of 342. A search of the literature revealed that both Kipping [84] and Metz [86] reported the formation of a compound known as 'Truxene' or 10,15-Dihydro-5H-diindeno[1,2-a;1',2'-c] - fluorene (193) which has a relative molecular mass of 342.

In the case of Metz [86] ,this compound was formed as a byproduct in the production of 1-indanone (132) from hydrocinnamic acid, in the presence of polyphosphoric acid.



(193)

To confirm that 'Truxene' arose as a direct result of acid-catalysed condensation of 1-indanone (132), a control experiment was carried out in which 1-indanone (132) was heated with p-tosic acid in refluxing toluene.
After 48 hours, yellow crystals which had a relative molecular mass of 342 were obtained ,
together with a fawn solid which had a relative molecular mass of 356.

A similar experiment using 2-indanone (168) in place of 1-indanone (132) afforded a pale green solid, which had a relative molecular mass of 360.
It appears that when 1-indanone (132) is heated in refluxing toluene with p-tosic acid, high molecular weight compounds of unknown structure are formed , as shown by mass spectrometry (Appendix 1.11 ; 1.12)

The elemental analysis data obtained for synthesised Truxene (193) was excellent, confirming that the relative molecular mass of the compound formed by the self-condensation of 1-indanone (132) in the presence of p-tosic acid in refluxing toluene is 342, that it has a molecular formula of $C_{27}H_{18}$ and that the compound is authentic 'Truxene' or 10,15-Dihydro-5H-diindeno[1,2-a;1',2'-c]-fluorene (193).

The elemental analysis data obtained for the compounds with relative molecular masses of 356 and 360 was inconclusive, and structures could not be assigned to these compounds.

As referred to on pages 85 and 96 , when the reaction between 1-indanone (132) and the amides -propionamide, benzamide and cinnamamide failed to give the desired enamidoindenylindenes, Truxene was obtained, as evidenced by Mass Spectra (appendix 1.11).

When 1-indanone (132) was heated for 4 days with p-tosic acid in refluxing toluene, truxene (193) was obtained in very poor yield (1%).

Time-controlled experiments were carried out where 1-indanone (132) was refluxed with acid for a short period of time (2 days) and a long period of time (7 days).

After heating for 2 days, the dicondensation product-2(1'-indanylidene)indan-1-one (189) was obtained in 95% yield.

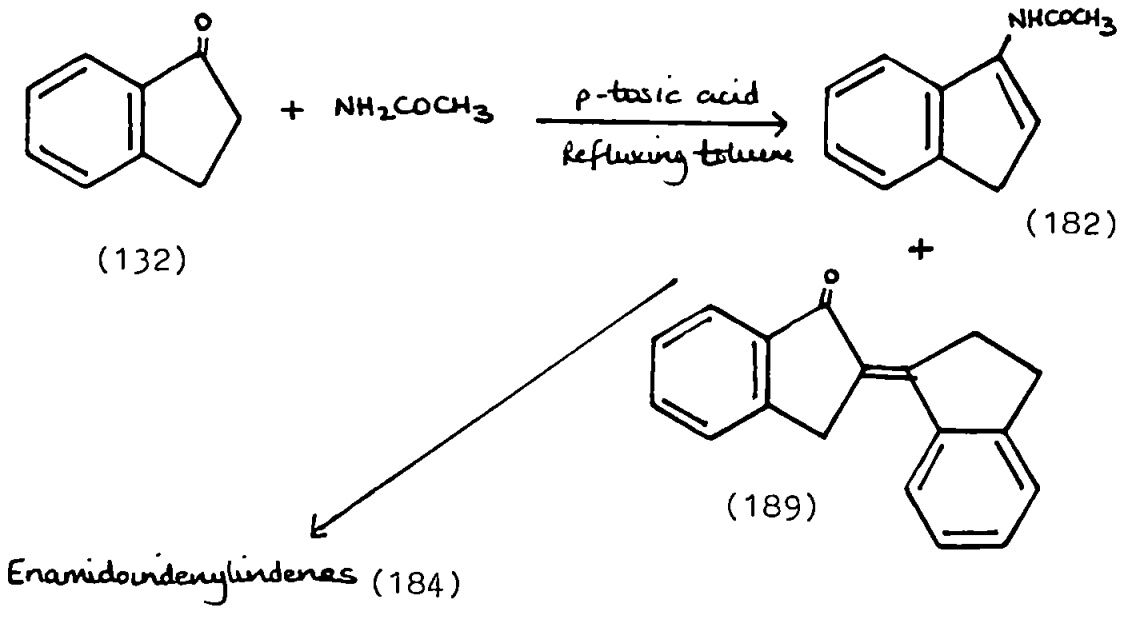
After 7 days, however, two products were obtained. These were the dicondensation ketone (189) in 25% yield, and truxene (193), obtained in 65% yield.

It therefore appears that the product obtained on self-condensation of 1-indanone (132) is dependent on time.

To verify that this is what occurs, a further experiment was carried out where 2(1'-indanylidene)indan-1-one (189) was heated for 5 days in refluxing toluene, in the presence of p-tosic acid.

The major product on cooling was truxene (193) with some unreacted ketone (189).

The evidence suggests that when 1-indanone (132) and an amide are heated together in the presence of p-tosic acid, two competing reactions occur. One leads to the formation of enamidoindenylindenes, the other leads to the formation of truxene (193). Scheme 123.



Scheme 123

Earlier in the chapter, it was noted that 2-acetamidoindene (183) had been synthesised in yields of upto 46%. Having investigated the routes to the various dimer-type products, attention was turned to making some more 2-acetamidoindene (183) with a view to investigating the Vilsmeier-Haack formylation.

A significant amount of 2-indanone (168) was prepared by the method of Rosen, Dorfman and Linfield,[89] as opposed to the customary practice of using the material from Aldrich, either as received or purified by steam distillation.

However, the reaction between acetamide and the new 2-indanone (168) failed.

At the same time (Feb 1990), Miss A Homfray[90] was attempting to make some 2-acetamidoindene (183) as part of her BSc undergraduate research project and had noted that the condensation reaction worked if crude commercial 2-indanone (132) was used, but failed if purified material was employed.

Homfray[90] showed, using T L C, that commercial 2-indanone (168) contained 2 additional impurities which were not identified.

It seemed that 2-acetamidoindene (183) was produced via an impurity in the commercial indanone. The impurity and its effects are not known.

Several of the acid catalysed reactions of 2-indanone (168) previously referred to, were repeated using pure 2-indanone and were found to work as described, indicating that the conclusions of this part of the work were sound.

Due to this rather unusual circumstance, the Vilsmeier-Haack work was discontinued, as there was little point in continuing work where the availability of the starting material (2-acetamidoindene (183)), was uncertain, to say the least.

In addition, as two viable, low cost syntheses to indenopyridines (DuPriest et al[24]; Alves et al[62]) had recently been published, it was decided to look at a variety of indenopyridines made by these routes and, time allowing, return to the problem of the synthesis of 2-acetamido-indene later.

In 1992, the preparation of 2-acetamidoindene(183) was again repeated using commercially supplied 2-indanone (168)-Aldrich, used as received.

The desired 2-acetamidoindene (183) was obtained in very low yield (7 %).Repetition of this experiment using pure 2-indanone was unsuccessful.

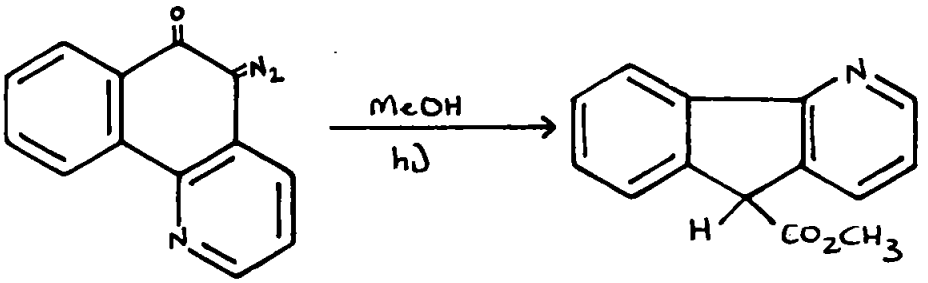
Again, it appears that (183) was produced via an impurity in the commercial indanone.

2-Indanone (168) was synthesised in bulk and allowed to 'age'. Experiments were carried out,approximately every 5 days, between acetamide and 2-indanone (168) in refluxing toluene. The last experiment was carried out using 99-day old indanone.On no occasion was 2-acetamidoindene (183) produced.

The lack of time prevented any further attempts to try to resolve this problem.It is evident, therefore, that these reactions warrant further investigation.

Chapter 9. Attempted Synthesis of Indenopyridines By The Wolff Rearrangement of Diazoketones.

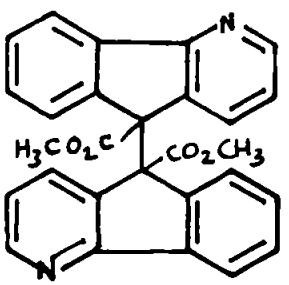
An alternative potential route to derivatives of 5H-indeno-[1,2-b]pyridin-5-one (8) involves the Wolff rearrangement of benz[h]quinolin-5,6-diazoketone (186).
Following the work of Süs et al[91], Smith[77] photolysed (186) in the presence of methanol in an attempt to prepare the methyl ester (187).Scheme 124.



(186) (187)

Scheme 124

Flash chromatography of the resulting reaction mixture afforded a solid instead of the oil expected for the methyl ester (bp 169-175°C)[77],(187).Following full characterisation of this solid, Smith[77] assigned it the structure of the dimer bis-5,5'(methyl 5H-indeno[1,2-b]pyridin-5-carboxylate), (194).



(194)

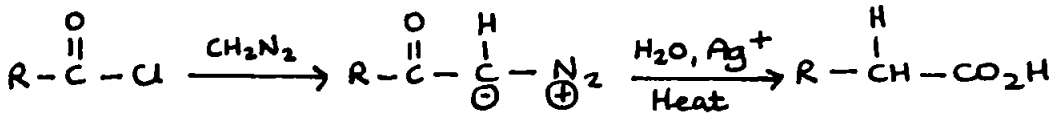
Smith[77] proposed that, assuming (187) is photolabile,(194) may arise by homolytic cleavage of the C5-H bond of methyl 5H-indeno[1,2-b]pyridin-5-carboxylate (187), followed by recombination of the radicals.

Further attempts by Smith[77] to obtain (187), both by photolysis and thermal decomposition, failed. Complex mixtures were obtained from the reaction from which neither the dimer (194), nor the required methyl ester (187) could be isolated.

As Smith[77] did not investigate alternative reaction conditions which might prevent dimer formation, it was decided to carry out a detailed investigation to find conditions under which rearrangement occurs, without dimerisation, to afford the desired compound, (187).

The Wolff rearrangement.

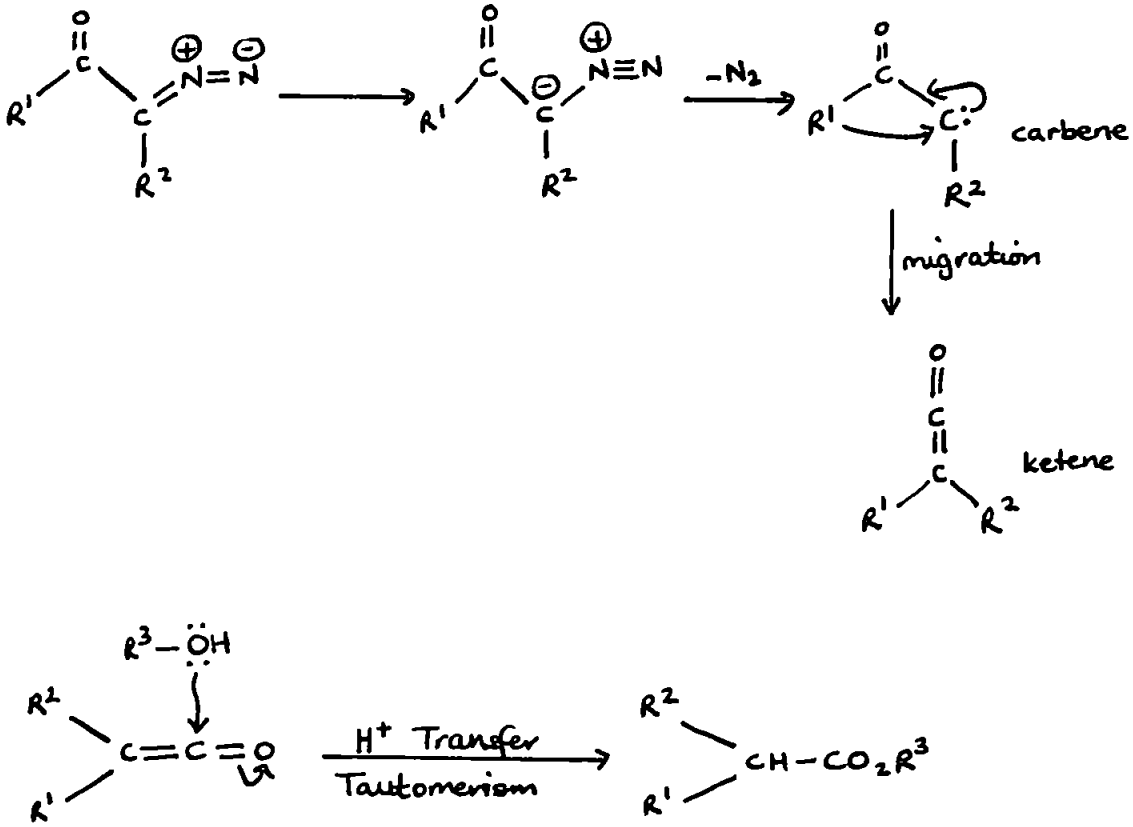
The Arndt-Eistert synthesis[92], involving reaction of an acid chloride with diazomethane followed by the rearrangement of the resulting diazoketone, has become a well established and useful method for converting an acid into it's next higher homologue.



The last step in the synthesis is the Wolff rearrangement which can be induced by thermolysis, photolysis or catalysis by Ag^+ ions.

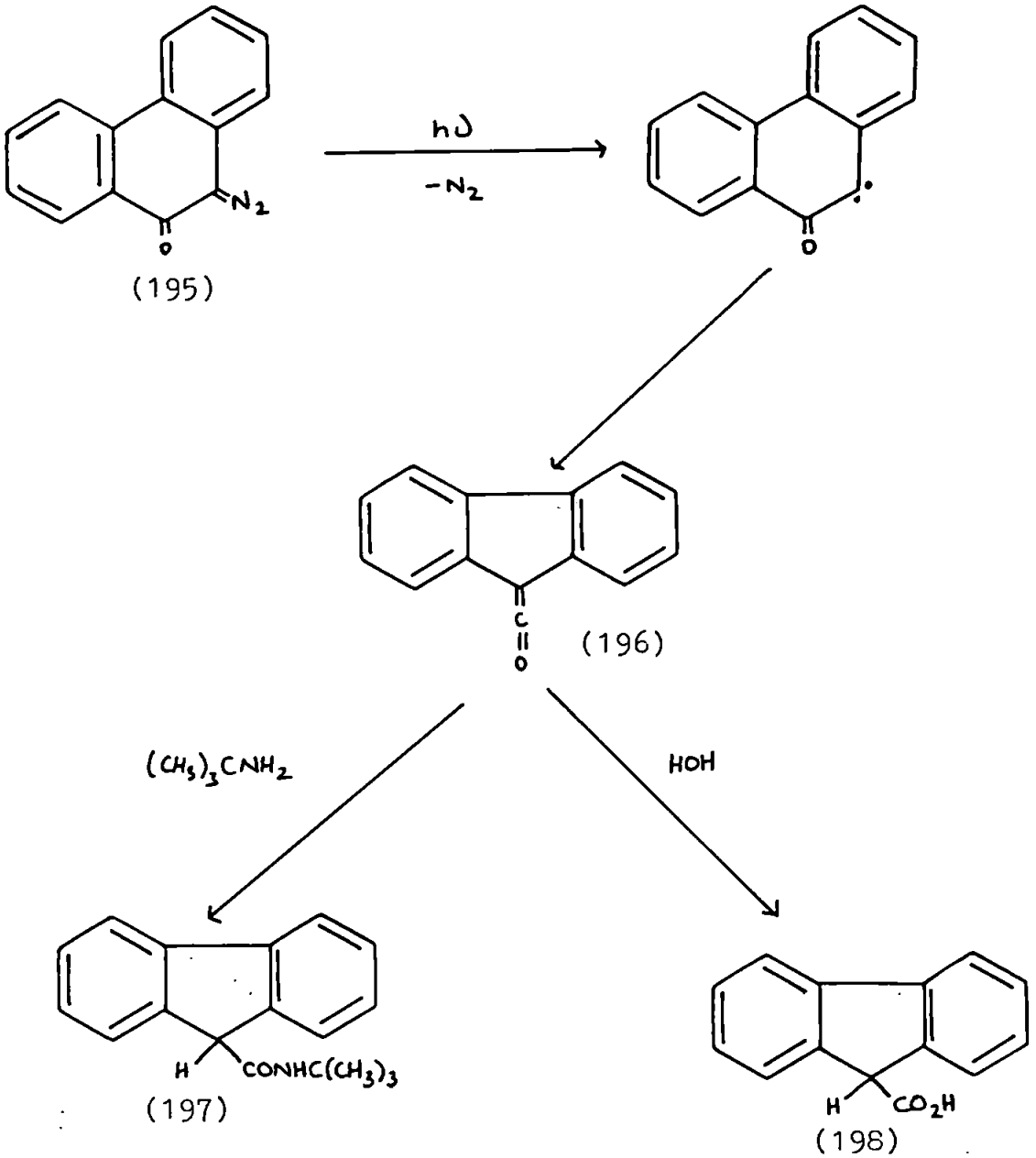
The Wolff rearrangement has been known for 70 years and is specific to α-diazoketones. It involves the conversion of α-diazoketones into acids and their derivatives when induced by the methods mentioned above.

Invariably, the reaction is carried out in the presence of water, alcohols or aqueous ammonia when the product is the carboxylic acid, ester or amides resulting from attack of the solvent on the ketene intermediate produced by the migration step[93](Scheme 125).



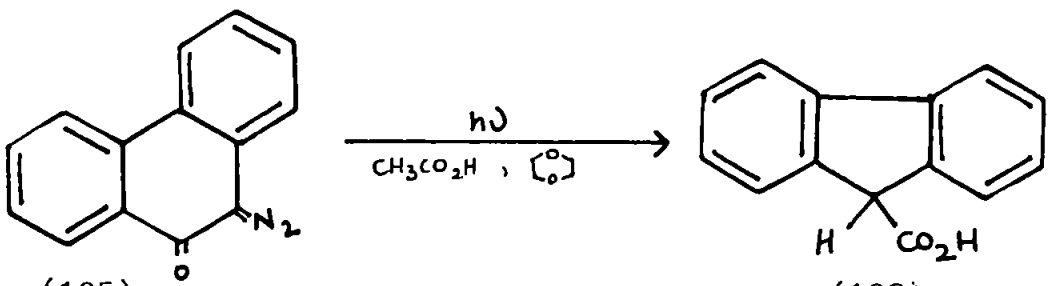
Scheme 125

The formation of ketenes in the rearrangement of diazoketones had been demonstrated experimentelly in several cases, and although they themselves are not isolated products of their further transformations are. This is illustrated for phenanthrene-9,10-diazoketone (195),which is shown in the preferred S-Z conformation.Reaction of the ketene (196) in the presence of tertbutylamine produces the amide (197), whilst the reaction in the presence of water gave the carboxylic acid (198).Scheme 126.



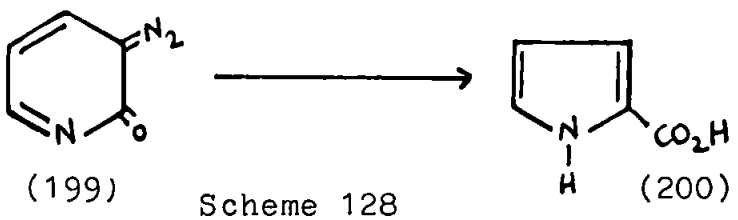
Scheme 126

Apart from the Arndt-Eistert homologisation, the main application of the Wolff rearrangement is ring contraction. As demonstrated by Süs[94,95] the Wolff rearrangement can be used with o-quinone diazides where ring contraction occurs providing access to the cyclopentadiene series; this is sometimes referred to as the Süs reaction[94,95]. For example, Süs et al[96] prepared fluorene-9-carboxylic acid (198) in 80-88% yield by the photolysis of phenanthrene-9,10-diazoketone (195) in aqueous dioxan containing acetic acid. Scheme 127.



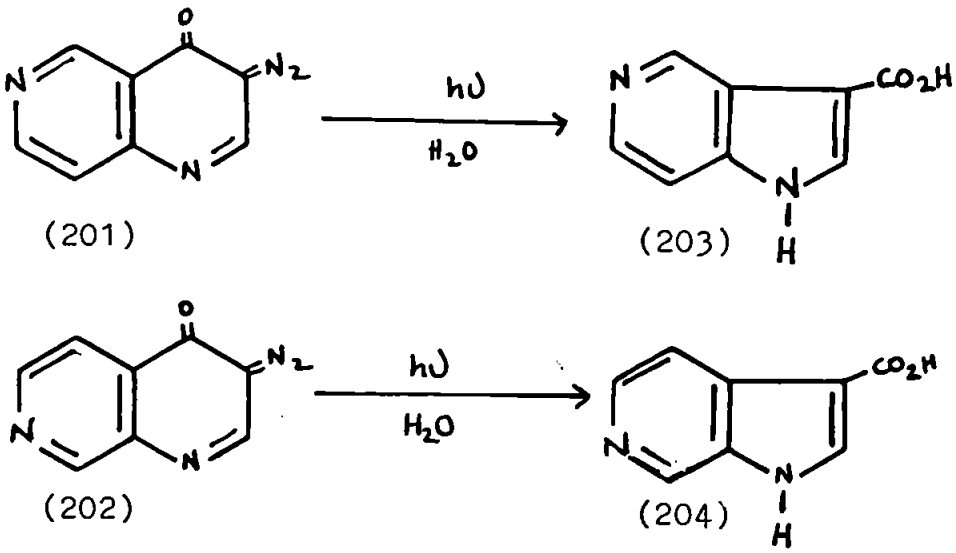
(195) Scheme 127 (198)

It appears that Süs[97] was the first to apply the Wolff rearrangement to heterocyclic α-diazoketones in 1953. For example, photolysis of 3-diazo-2,3-dihydro-2-oxopyridine (199) gave pyrrole-2-carboxylic acid (200), Scheme 128.



(199) Scheme 128 (200)

Similarly, photolysis of 3-diazo-3,4-dihydro-4-oxo-1,6(&7)-diazanaphthalenes (201,202) gave the corresponding 1,5(&6)-di-azaindene-3-carboxylic acids (203,204) in 50% yields[97]. Scheme 129.

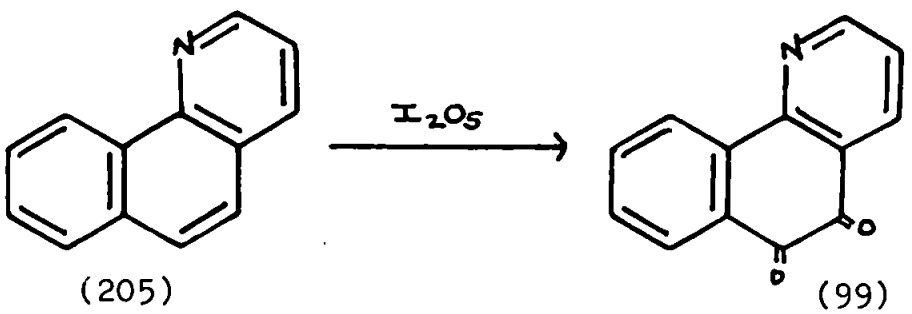


(201) (203)

(202) (204)

Scheme 129

The starting material required for the present study was the dione : benz[h]quinolin-5,6-dione (99).This was prepared using the method of Kloc et al [17], by oxidation of the corresponding benzoquinoline (205) with iodine pentoxide.Scheme 130.



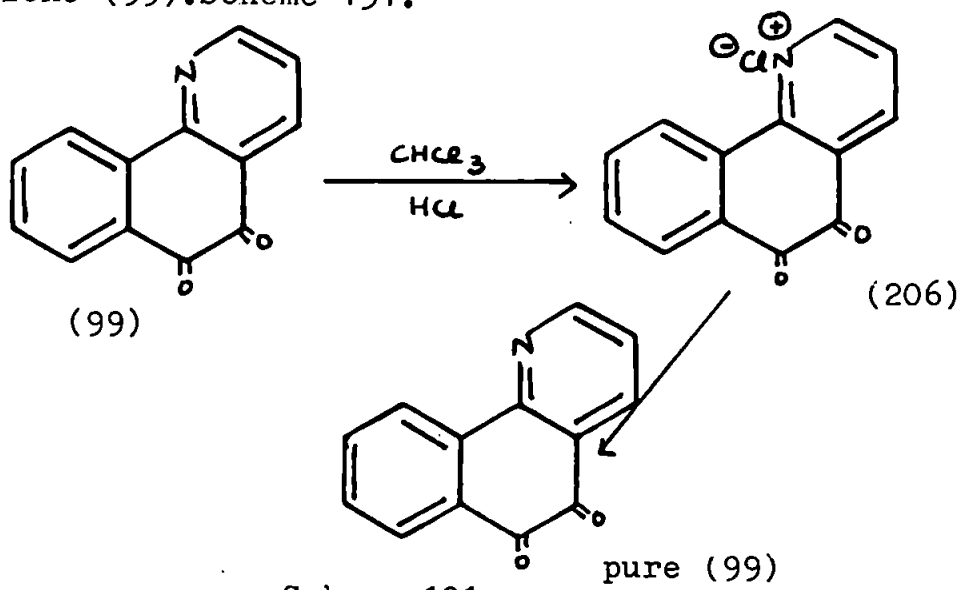
(205) (99)

Scheme 130

The dione was purified by extraction into chloroform. Recrystallisation from ethanol afforded the pure dione (99) in 40% yield.

An alternative procedure for purification of the dione, also by Kloc et al [31], involved dissolving the dione in benzene.

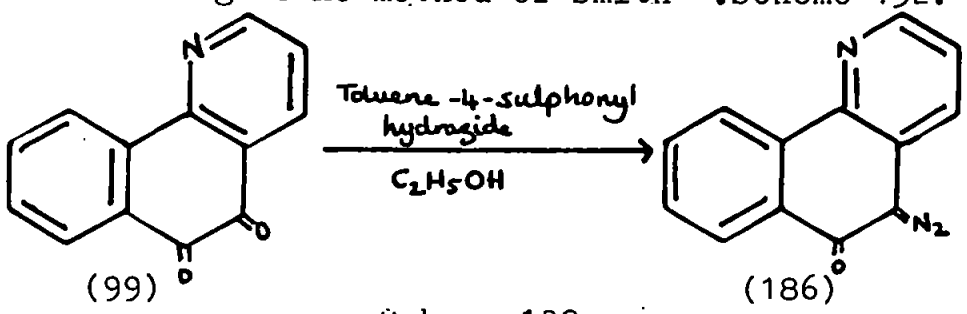
The benzene, together with any remaining iodine, was then distilled off and this was repeated until the distillate was colourless. The product was then decolorised with charcoal. Recrystallisation from ethanol afforded the pure dione (99). Using this method, however, yields were reduced to 35%. It was thought that the preparation of 5,6-dioxobenz[h]-quinolinium chloride (206) might be used to purify the dione (99). Scheme 131.



Scheme 131

The dione was removed as a salt (206) and the free bases being released on recrystallisation from acetonitrile. This proved to be a good method, benz[h]quinolin-5,6-dione (99) being obtained in 62% yield. This method was therefore used for purification of the dione.

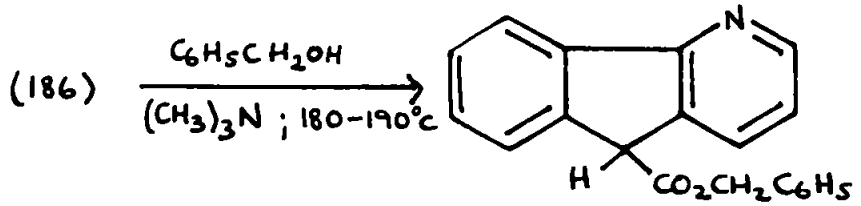
Benz[h]quinolin-5,6-diazoketone (186) was prepared in 75% yield according to the method of Smith[77]. Scheme 132.



Scheme 132

Attempted rearrangement by Thermolysis.

Initial attempts were made to produce the indenopyridine - benzyl 5H-indeno[1,2-b]pyridin-5-carboxylate (207) by thermolysis of benz[h]quinolin-5,6-diazoketone (186) in the presence of benzyl alcohol.Scheme 133.



Scheme 133 (207)

It was thought that the large benzyl group might prevent dimerisation, which was observed by Smith[77] with the small methyl group.

Wilds and Meader[98] also state that the most efficient thermal procedures involved decomposition of the diazoketone in benzyl alcohol.

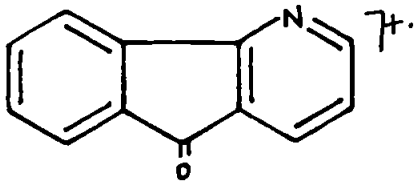
The rearrangement was, therefore, attempted in benzyl alcohol with triethylamine as the tertiary base.The tertiary amine may increase the yields of product in thermal rearrangements[98].

Nitrogen evolution was rapid when the reaction solution was placed in an oil bath at 180°C and after 5 minutes nitrogen evolution ceased, indicating that the reaction was complete. Preparative T L C showed that four products had been formed. The products were separated by flash chromatography, the initial eluent was ethyl acetate (5%) and petroleum spirit (95%) with the ratio of ethyl acetate being gradually increased to 10%.The fractions were collected and examined by T.L.C. and those containing solutes with similar Rf values were combined.

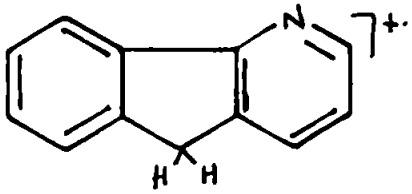
As evidenced by infrared spectroscopy, of the four fractions that were obtained, only two fractions (fractions 3 and 4) contained an ester carbonyl absorption (ν C=O 1740 and 1715 cm^{-1} respectively).

Mass spectral analysis showed that these fractions also contained indenopyridine fragments indicative of the desired product (207)(Appendix 1.16 and 1.17).

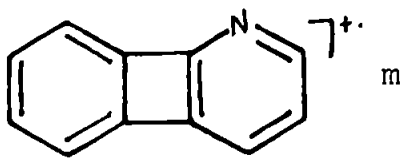
Smith's work[77] indicates that indenopyridines have a recognizable fragmentation pattern. Mass spectral features indicating the presence of indenopyridines are shown below :



m/z 181

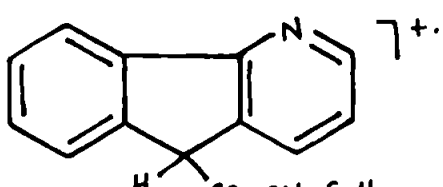


m/z 167

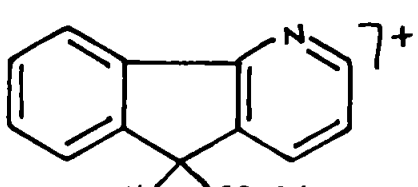


m/z 153

The last fraction (fraction 4) had the aforementioned fragments as well as other fragments indicative of the desired product (207).These fragments had m/z 224 and m/z 301 (appendix 1.17) whose suggested structures are indicated below.



m/z 301



m/z 224

From mass spectral analysis, there is no evidence of dimer formation.

Attempts to purify fraction 4 by flash chromatography, however, proved unsuccessful.

Repetition of this experiment gave several products. Again, attempts to purify the final fractions were unsuccessful.

Rearrangement was then tried by reacting the diazoketone (186) in refluxing ethanol with the tertiary amine, triethylamine. After reaction was complete, the product was examined by T L C which indicated two components, starting material and putative product. Removal of the solvent, however, gave 87% recovery of the diazoketone (186), only. This reaction was not pursued further.

Heating the diazoketone (186) in refluxing ethanol for 9 hours, in the absence of triethylamine also proved to be unsuccessful. The starting material was recovered in 93% yield.

The same also occurred in benzyl alcohol T L C examination of the reaction solution indicated no change. The reaction mixture was then divided into two.

The first half of the solution was acidified and extracted into chloroform.

T.L.C. examination indicated four products which were isolated by preparative T.L.C., the bands which resulted were scraped from the plates and placed in centrifuge tubes.

They were extracted with chloroform by centrifuging for 15 minutes at 1.5 x 1000 ↻/min.

Infrared examination of the resulting four fractions indicated that no carbonyl ester group was present; mass spectral analysis showed that no indenopyridine fragments (m/z 181,166,154) were present.

The second half of the reaction mixture was subjected to ultrasonication which had no effect on the diazoketone (186).

Summary.

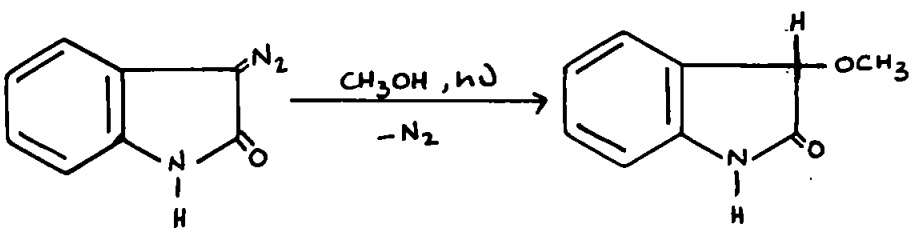
Initial attempts to rearrange benz[h]quinolin-5,6-diazoketone (186) by thermolysis proved promising. Purification by T L C of the reaction mixture gave several fractions; each fraction contained several components, which when examined by mass spectrometry suggested that the desired indenopyridine (207) was present. However, attempts to purify these fractions by flash chrometography proved fruitless.

Rearrangement by Photolysis.

As attempts to obtain indenopyridines by the Wolff rearrangement of (186) under thermal conditions proved unsuccessful, attention was turned to the use of photolysis to induce rearrangement.

Photolysis, originally discovered by Horner[99], is the more superior method for the Wolff rearrangement, normally succeeding where thermal and catalytic approaches merely resulted in C-H insertion.

α-Oxo carbenes arising as intermediates in the Wolff rearrangement may insert into C-H, C-C ,C-O , O-H bonds. For example, compound (208) does not undergo rearrangement by irradiation , but insertion instead[100].Scheme 134.



(208)

Scheme 134

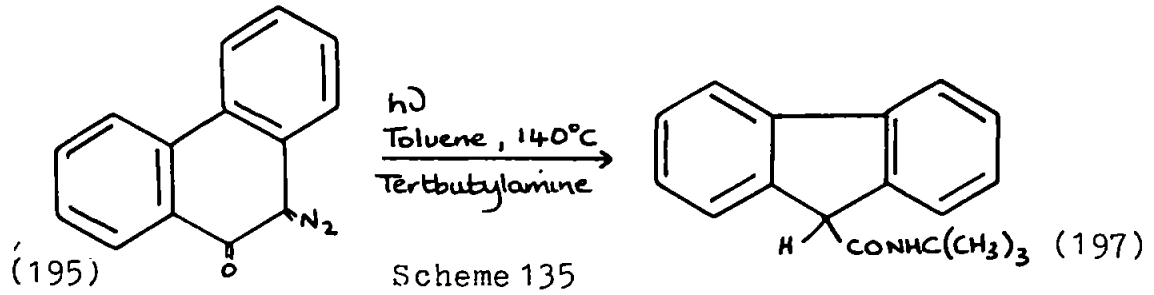
The limit of photolysis is reached when the product itself is photolabile under the irradiation conditions.[99]

There are considerable advantages in inducing the Wolff rearrangement by photolysis.These include mild reaction conditions. The experiments are, practically , fairly simple and there is a reduction in the possibility of side reactions.

The wavelength chosen should be as long as possible and for as short a time as possible. Decreasing the wavelength ,ie increasing the energy of the radiation, leads to an increase in the amount of byproducts produced.

In order to establish reliable experimental conditions for the photolysis of benz[h]quinolin-5,6-diazoketone (186), the analogous carbocyclic compound, 9-diazo-10-phenanthrone (195) was photolysed.

Kinson and Trost[101] have reported the synthesis of (197) by rearrangement of the diazoketone (195), Scheme 135.



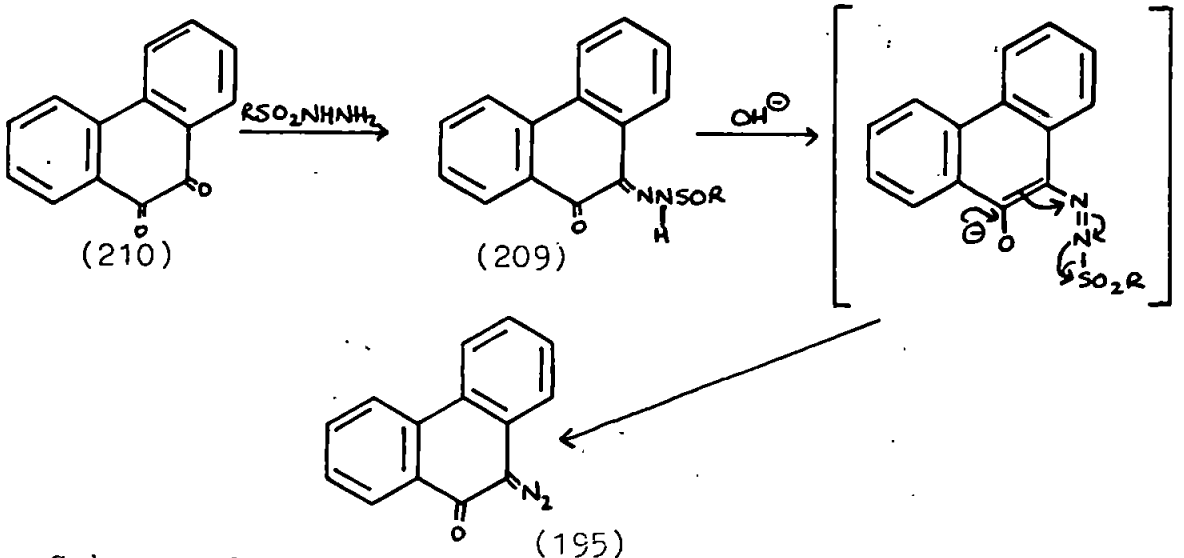
(195) (197)

Scheme 135

However, no experimental data nor physical properties for (197) were given. This rearrangement was therefore re-investigated to establish reliable conditions.

The diazoketone (195) was obtained in good yield by the reaction of 9,10-phenanthraquinone with toluene-4-sulphonyl-hydrazide, using the method of Cava et al[102].

The tosylhydrazone (209) which is initially formed when the dione (210) reacts with toluene-4-sulphonylhydrazide decomposes spontaneously to give the diazoketone (195) in 53% yield. Scheme 136.



(210) (209) (195)

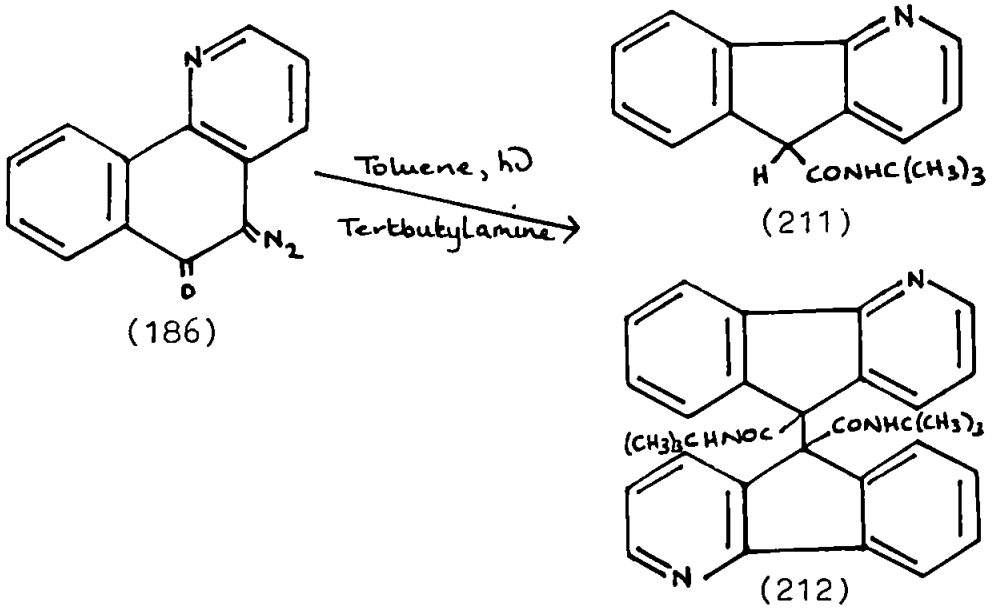
Scheme 136

9-diazo-10-phenanthrone (195) was dissolved in toluene together with tertbutylamine and was irradiated for 20 hours with a low pressure (LP) mercury lamp.The amide (197) was obtained in 86 % yield .Scheme 135.

Although there was a slight discrepancy in the elemental analysis (Found C 83.11,H 6.58 , N 4.89 ; Required C 81.50 , H , 7.17 , N 5.28), the identity of the amide (197) was confirmed as being 9H-fluorene-9N-tertbutylcarboxamide on the basis of spectral data (Infra-red,νN-H 3265 ;amide I & II 1650 & 1555cm^{-1};Mass Spectrum Appendix 1.19).The spectral properties of (197) have not been described previously.

The photolysis of benz[h]quinolin-5,6-diazoketone (186) was carried out in the same manner as that of (195).

(186) was dissolved in toluene together with tertbutylamine. The solution was irradiated at room temperature for 25 hours using a LP lamp. T L C examination of the solution showed that two components were present,which were assumed to be the starting material(Rf 0.37) and a small amount of material with Rf 0.62, possibly the required amide : 5H-indeno[1,2-b]pyridin-5N-tertbutylcarboxamide (211) or it's dimer (212).Scheme 137.

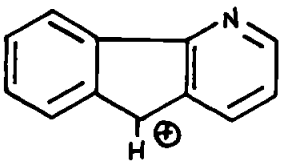


(186)

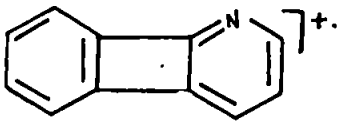
Scheme 137

In order to maximise the yield of the product (**211**), photolysis was continued for a further 24 hours, samples being taken every 5 hours and examined by T L C
All the samples contained two components (Rf 0.37 and 0.62), apart from the last sample which contained four components. The reaction was therefore stopped after 49 hours to prevent more products from being formed.
The last sample contained four components with Rf values of 0.15, 0.37 ,0.51 and 0.63. When the diazoketone (**186**) was dissolved in toluene, to provide a sample for T L C analysis, only one component was initially observed (Rf 0.37), but on leaving the solution for several hours in daylight, two components were observed (Rf 0.37 and 0.51).
These two components were also observed on the photolysis of the diazoketone (**186**) as evidenced by T.L C

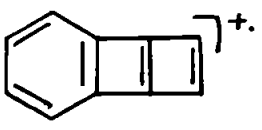
The two other components found in the last sample had Rf values of 0.63 and 0.15. These were separated by preparative T L C and extracted into chloroform.
Infrared examination of these compounds showed that no carbonyl stretching frequencies were present. If the amide (**211**) were present a carbonyl stretching frequency would be expected at ca. 1650 cm^{-1}.
Mass spectral examination also indicated that the desired product was not present, as fragments expected from the amide were not observed. Such fragments would be :



M/Z 166



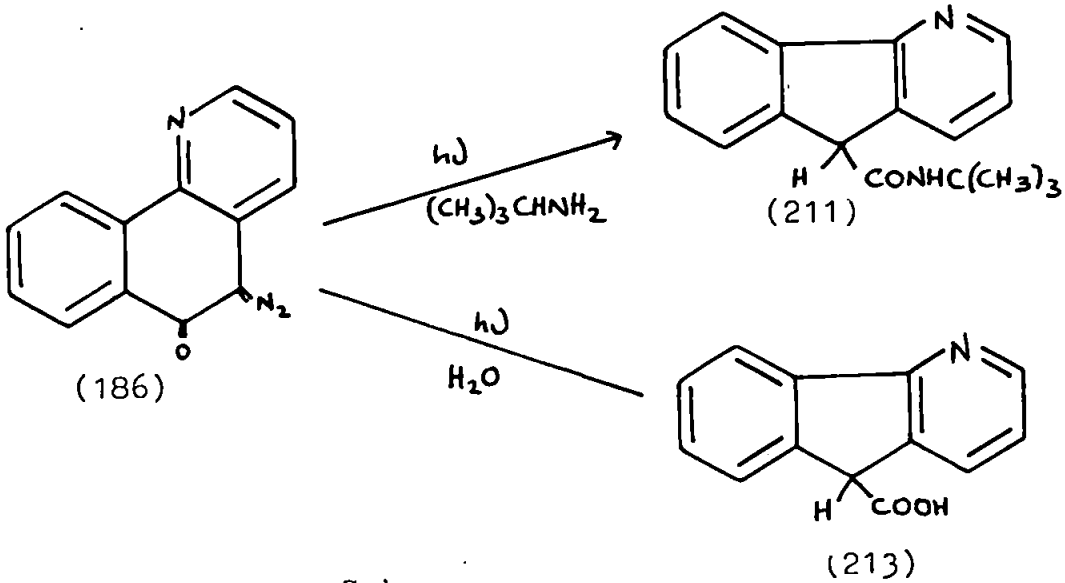
M/Z 153



M/Z 126

A solid which was scraped from the photolysis tube, after it had been removed from the reaction solution, was found to be the starting diazoketone (186).

The photolysis of (186) in the presence of tertbutylamine was repeated at a temperature of 40°C and for a longer period (72 hours) to see if this would effect rearrangement.
A leak in the apparatus, however, led to the introduction of water. Instead of the amide (211) being formed, it may be possible that the acid 5H-indeno[1,2-b]pyridin-5-carboxylic acid (213) was formed .Scheme 138.



(186) (211) (213)

Scheme 138

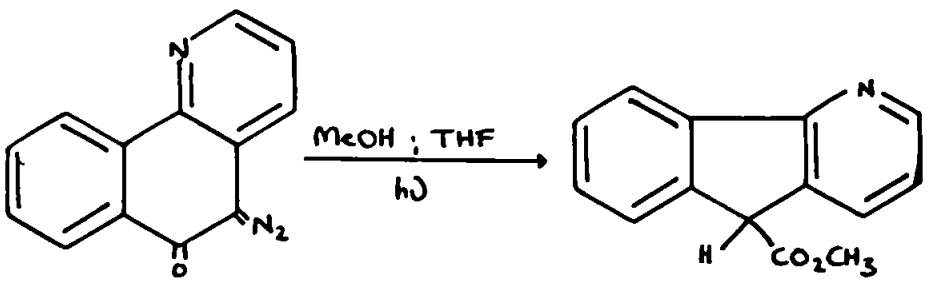
The two layers that resulted from the introduction of water were collected.The aqueous layer was found to contain only one component which had a Rf of 0.08. Examination by infra red and mass spectra., indicated that neither the amide nor the carboxylic acid were present.
The toluene layer contained three components with Rf values of 0.62 ; 0.46 and 0.36, the latter being starting material. The component with a Rf of 0.62 was shown not to contain any of the desired product, as evidenced by infrared and mass

spectra. The infrared spectra contained no ∂C=O stretching frequencies and the mass spectrum showed no fragments indicative of an indenopyridine structure.

The other component (Rf 0.46) had mass fragments at m/z 154 and m/z 183 (Appendix 1.20) but the desired products (211 , 213) were not observed. This was confirmed by infrared spectroscopy which showed that no amide or carboxylic ∂C=O stretching frequencies were present.

It appears that although the Wolff rearrangement proceeded easily with 9-diazo-10-phenanthrone (195) in toluene, rearrangement with benz[h]quinolin-5,6-diazoketone (186) was unsuccessful.

An attempt was therefore made to repeat the photolysis experiment of Smith[77], using methanol and tetrahydrofuran as solvents, to produce methyl 5H-indeno[1,2-b]pyridin-5-carboxylate (187), Scheme 139 .



(186) (187)

Scheme 139

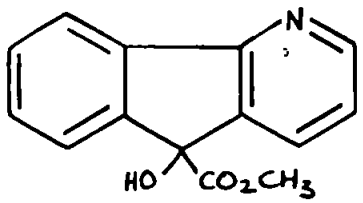
Two experiments were performed. In the first experiment, the solution was irradiated for 34 hours using a LP lamp. Examination of the cooled reaction mixture by T L C indicated that three products were present (Rf 0.66 ; 0.55 ; 0.42).

The second experiment involved, initially, irradiating the solution for 8 hours with a LP lamp. The solution was then irradiated further using a High Pressure (HP) lamp (125W) for 24 hours. T.L.C. examination showed that three products were present with Rfs 0.66 ; 0.42 and 0.26 .

The different components in each experiment were isolated by preparative T L C and those with the same Rf values were combined.

From mass spectral examination, the components with Rf values 0.66 ; 0.55 and 0.42 all contained fragments at m/z 181 and m/z 153 which are indicative of an indenopyridine.

The component with Rf 0.55 also contained a fragment at m/z 241 , which is the mass of the possible product (214), whose structure is suggested below. (Appendix 1·21)



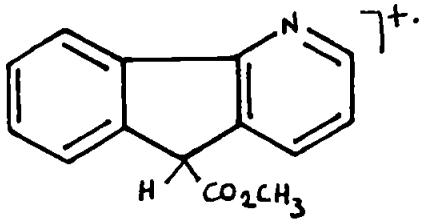
(214)

The component with Rf 0.42 contained a fragment at m/z 448. This could be the dimer that Smith[77] produced when he performed this experiment, bis-5,5'(methyl-5H-indeno-[1,2-b]pyridin-5-carboxylate) , (194). Infrared examination indicated the presence of the dimer (ν C=O 1730 cm^{-1}) ; ($M^{+\bullet}$ 448 -appendix 1·22)

Attempts to isolate the separate components by flash chromatography of the reaction solution, using a mobile phase of petroleum ether (40-60) and ethyl acetate, proved unsuccessful.

The above experiment was repeated at temperatures of 0°C and 40°C, to see if temperature had any effect on the rearrangement.

At 0°C, three components were observed by TLC examination. The components had Rf values of 0.55 ,0.42 and 0.26. All three were found to contain mass fragments indicative of an indenopyridine structure when examined by mass spectra. All the components contained a mass fragment as m/z 225 (appendix 1.21, 1.22, 1.23), which might have the structure indicated below, (187).



(187)

The component with Rf 0.42 also contained a m/z 448 (appendix 1. 22), which might be the dimer (194). Attempts to isolate the above components by flash chromatography were unsuccessful.

At 40°C, photolysis produced 3 products, which were, however different from those products formed by photolysis at 0°C, as observed by their Rf values of 0.77, 0.57 and 0.18. The latter product (0.18) did not contain any mass fragments indicative of an indenopyridine.

The other two products produced on photolysis (Rf 0.57 and 0.77) contained mass fragments indicative of an indenopyridine (as evidenced by mass spectra), both fractions also having m/z at 225 which might, again, have the above structure (187). Appendix 1.24 and 1. 25 respectively.

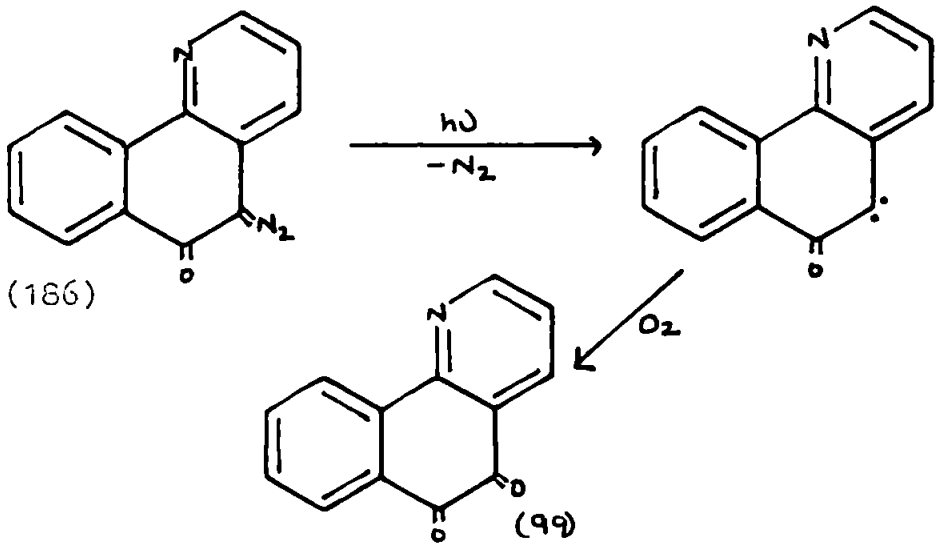
Further attempts to purify this compound, assumed to be the desired product (**187**) by flash chromatography proved fruitless.

As photolysis of the diazoketone (**186**) in methanol and tetrahydrofuran produced a small amount of product (both monomer and dimer , **187** and **194** respectively) which could not be purified to give analytical samples, attempts to photolyse the diazoketone (**186**) using the initial solvent of toluene, with tertbutylamine as the tertiary amine, were made. This time , however, a HP lamp was used(the HP lamp has a much more intense arc and irradiates predominantly at 365-366 nm , with smaller amounts in the UV and visible range).

After 4 hours, irradiation was stopped and examination of the reaction solution showed that apart from the starting material (**186**) , only one other component was present. Infrared examination showed that no carbonyl absorptions were present,the conclusion that this compound was not the desired amide , was confirmed by mass spectral examination.

All the experiments conducted so far produced only a small amount of the desired product,if any at all.
The other 'products' present at the end of the photolysis must, presumably, have been produced by the breakdown of the diazoketone (**186**) ,or by alternative reactions occurring at the ketene stage.Such reactions might include a [1,2-H] shift at the ketene stage to produce an unsaturated ketone, or an insertion reaction[99].

It is possible that oxidation of the intermediate carbenones might have occurred, where only the dione (99) was isolated after illumination[102]. Scheme 140 .



Scheme 140

The latter seems improbable as the dione produces characteristic mass ion, $M^{+\bullet}$ 209. This ion, does not appear on any of the mass spectra obtained for the components that are produced on photolysis.

This was confirmed experimentally. Irradiation of the dione (99), in methanol and tetrahydrofuran, with a HP lamp resulted in only the starting material being recovered. It must be concluded therefore, that the dione (99) is unaffected by UV radiation.

It is probable that the components obtained after photolysis, are a result of the breakdown of the diazoketone (as expected) This was confirmed by the characteristic mass fragment of m/z 193 being observed in most of the mass spectra obtained for said components.

Summary.

It has been confirmed experimentally ,that 9-diazo-10-phenanthrone (**195**) does rearrange to give the amide 9H-fluorene-9-N-tertbutylcarboxamide (**197**) in good yield.

Although irradiation of the diazoketone (**186**) under the same conditions as above was unsuccessful, rearrangement in the methanol/tetrahydrofuran solvent system looked promising. Mass spectral examination of the components obtained after photolysis indicated that both the monomer and the dimer (**187** and **194** respectively) were present.Attempts to isolate these compounds (**187**) and (**194**) by flash chromatography , however, were unsuccessful.

It might be useful to try adding a tertiary amine to the methanol/tetrahydrofuran system to see if rearrangement can be encouraged.Wilds and Meader[98] have stated that a tertiary amine is not essential for the Wolff rearrangement to occur; but it does help to increase the yield of the product.

Benz[h]quinolin-5,6-diazoketone (**186**) may not rearrange because of electronic deactivation.The electronic structure of the nitrogen analogue may deactivate the molecule,thus preventing it from rearranging.

Clearly further experimental work is necessary. Unfortunately constraints of time prevented further study of these reactions.

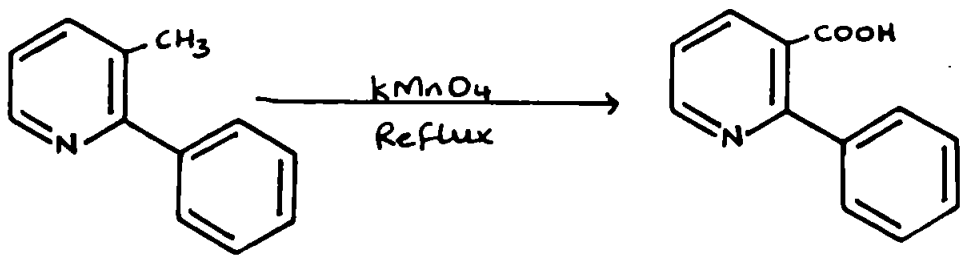
Chapter 10. Indenopyridines from 3-methyl-2-phenylpyridine

During the course of the previous work (Chapter 8 and 9) DuPriest et al[24] and Alves et al[62] both published novel, relatively low cost syntheses of indenopyridines.

As the attempted methods of formation of indenopyridines, via enamides and the Wolff rearrangement of benz[h]-quinolin-5,6-diazoketone (186), were proving unsuccessful, the method of DuPriest et al[24] was chosen in an attempt to produce a variety of indenopyridines whose chemistry could be studied.

This route appeared even more attractive since Key Organics (Camelford, Cornwall) were able to provide a supply of the starting material, 3-methyl-2-phenylpyridine (79).

Using DuPriest's method,[24] potassium permanganate oxidation of (79) produced the desired substituted 3-nicotinic acid: 2-phenyl-3pyridine carboxylic acid (158). Scheme 141.

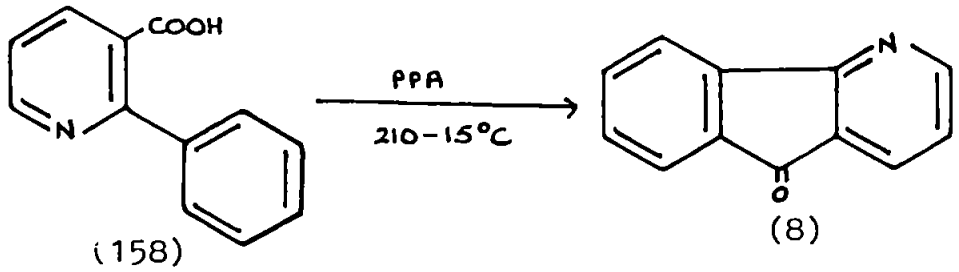


(79) (158)

Scheme 141

The method used involved continuous extraction with dichloromethane. Removal of the solvent afforded the acid (158) in good yield (87%).

The cyclisation of 2-phenyl-3-pyridinecarboxylic acid (158) in hot polyphosphoric acid at 210-15°C occurred smoothly to afford 5H-indeno[1,2-b]pyridine-5-one (8) in excellent yield (97%), Scheme 142.



(158) (8)

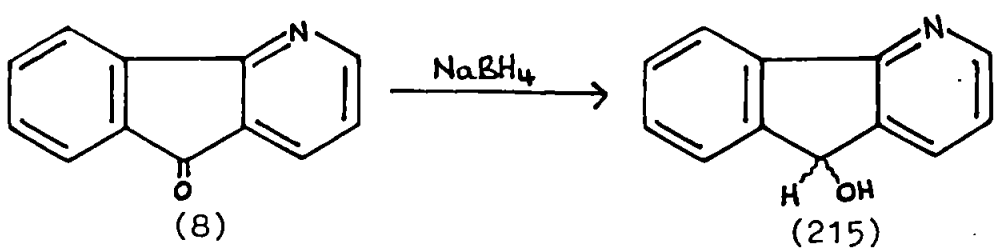
Scheme 142

The reaction had to be carefully controlled. If the temperature was not maintained between 210-15°C, the yield dropped to between 50 and 70% . Compound (8) was synthesized in bulk and used for all subsequent studies. Novel and known compounds were synthesized and their spectroscopic and chemical properties examined, thus increasing the knowledge of this fairly uncommon class of compound.

Reactions of the oxo group of 5H-indeno[1,2-b]pyridine-5-one(8)

Reduction of 5H-indeno[1,2-b]pyridine-5-one (8)

The known compound 5-hydroxy-5H- indeno[1,2-b]pyridine (215) was obtained in 83% yield by reduction of the oxo precursor (8) with sodium borohydride[77]. Scheme 143.

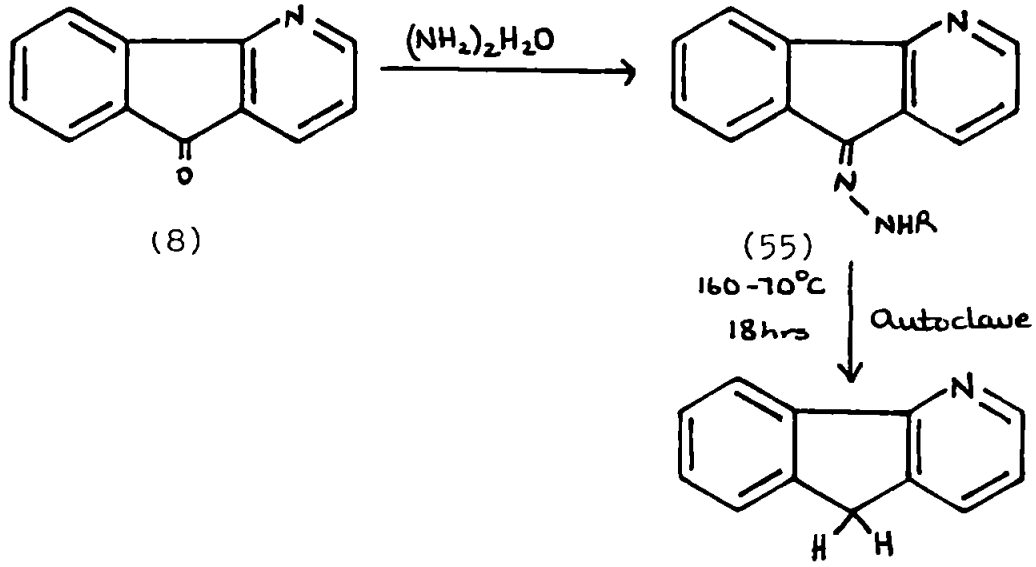


(8) (215)

Scheme 143

Attempts were then made to reduce the oxo compound (8) to the methylene analogue (4),using the conventional method, the Wolff-Kishner reduction.

Mlochowski and Szulc[32] have reported the above reduction using wolff-Kishner conditions, the intermediate being a hydrazone (55,R=H).Scheme 144.



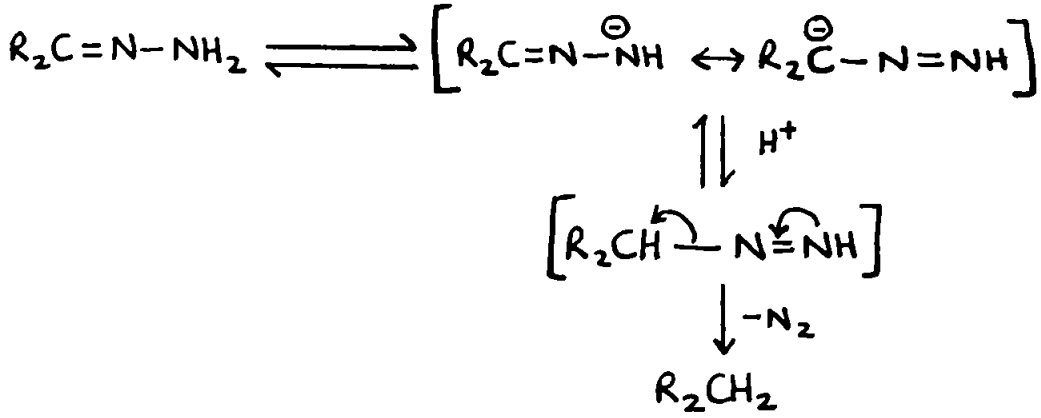
(8) (55) (4)

Scheme 144

The hydrazone (55,R=H) was obtained in good yield herein, (78%). The reduction method,however, involved heating the hydrazone in an autoclave for 18 hours. Since an autoclave was not available in the present study, this reaction method could not be taken to completion.

Attempts were then made to reduce the oxo compound (8) using the Huang-Minlon modification of the Wolff-Kishner reduction. In this method the hydrazone is formed by refluxing the carbonyl compound with hydrazine hydrate and potassium hydroxide in triethylene glycol.After completion of formation of the hydrazone, the condenser is removed and the water liberated in this first reaction is distilled.

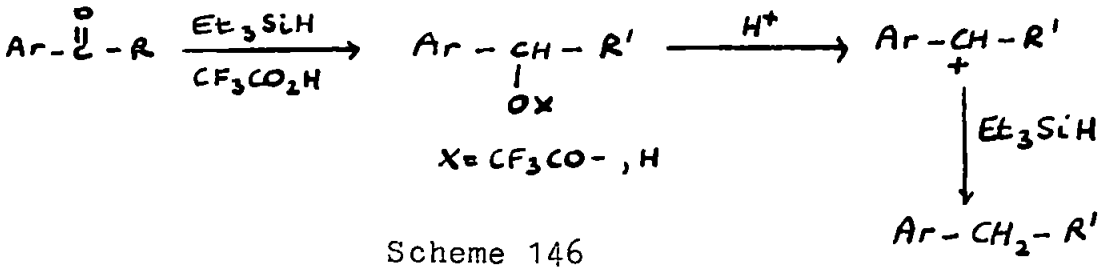
The temperature is allowed to rise to approximately 200°C, so bringing about decomposition of the hydrazone.Scheme 145.



Scheme 145

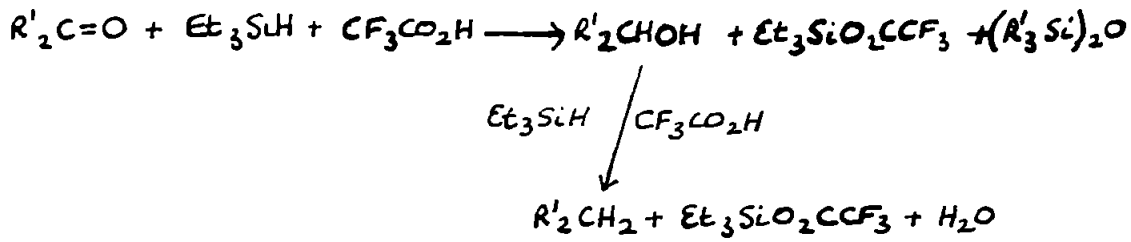
Following the Huang-Minlon modification,[103] 5H-indeno[1,2-b]-pyridin-5-one (8) was refluxed with hydrazine hydrate and potassium hydroxide in triethylene glycol for 45 minutes. Removal of the water and refluxing for a further 3 hours afforded a black coloured solution which was extracted with diethyl ether. Removal of the ether afforded a small amount of fawn solid and recrystallisation from toluene/methanol afforded the alcohol (RS) 5-hydroxy-5H-indeno[1,2-b] pyridine (215) in 20% yield, instead of the expected hydrocarbon (4).

An alternative method of reduction was next attempted, based on a method described by Maurer et al[104] which involves selective reduction of the carbonyl groups of arylcarbonyl compounds using triethylsilane (TES) in trifluoroacetic acid. Scheme 146.



Scheme 146

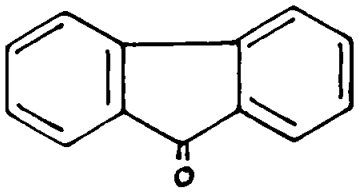
In general, two equivalents of silane are required for the reduction of one equivalent of carbonyl compound to the methylene product. Side reactions produce the silane products triethylsilyltrifluoroacetate and hexaethyldisiloxane. Scheme 147.



Scheme 147

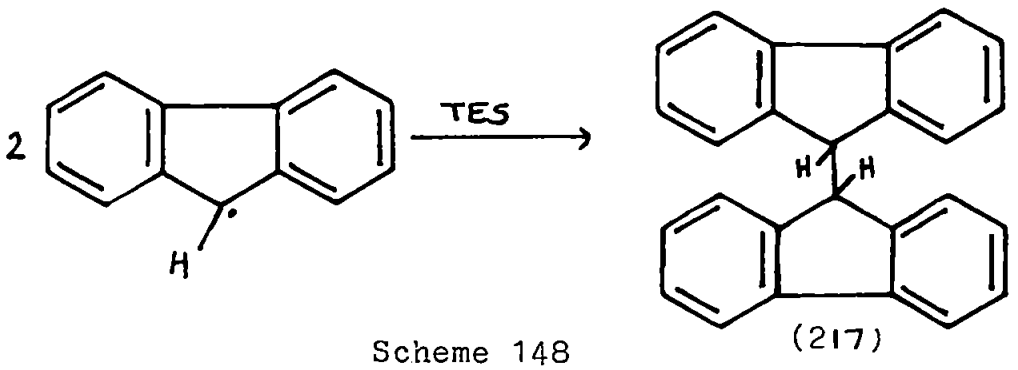
The ketone (8) was dissolved in trifluoroacetic acid and a little tetrachloromethane.Triethylsilane was added over 15 minutes and the solution was stirred for 24 hours at 45°C. After work-up of the reaction solution and extraction of the product into diethyl ether, removal of the solvent afforded the starting ketone with 56% recovered.
Repetition of this experiment led to 78% recovery of the starting ketone (8).

As reduction of the indenopyridone (8) did not occur using triethylsilane (TES), attempts were made to find the optimum conditions for reduction using fluorenone (216) as a model.



(216)

Fluorenone (216), when treated with triethylsilane as described above, afforded an unexpected dimer 9,9'-bifluorenyl (217) in 77% yield, confirmed by m.p.[105] The previous mechanism (Scheme 145, page 126) is an ionic one and does not describe how the dimer (217) might arise. Dimers normally arise from the recombination of radicals, as indicated below for fluorene. Scheme 148.



(217)

Scheme 148

Under the above reaction conditions (TES reduction), the fluorene radical maybe more stable than the indenopyridine radical. Therefore with fluorenone (216) the radicals combine to give the dimer (217); whereas with 5H-indeno-[1,2-b]pyridin-5-one (8), the radical is not formed, or if formed does not react and only the starting material is recovered.

As the conventional methods of reduction of the oxo compound (8) were unsuccessful, alternative methods to the methylene compound (4) were tried.

Reduction using red phosphorus and hydriodic acid, as used by Chatterjea and Prasad[46] was next attempted.

The oxo compound (8) and red phosphorus were refluxed together in hydriodic acid for 7 hours. On cooling, white needles of the hydroiodide of 5H-indeno[1,2-b]pyridine separated out. Treatment of the hydroiodide with sodium hydroxide afforded the free base (4) in 78% yield.

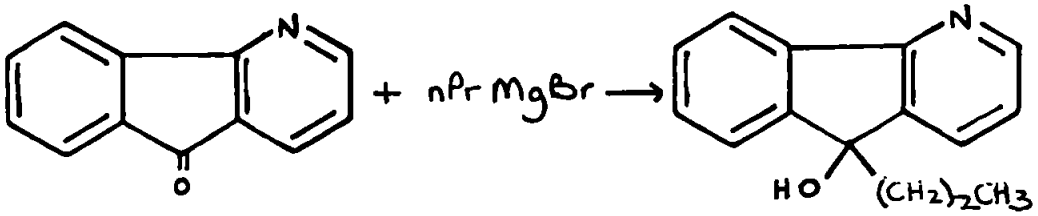
The oxo compound (8) was then reduced using the unconventional method of DuPriest et al[24] . This method maybe considered unconventional in that the method used is essentially a Huang-Minlon modification of the Wolff-Kishner reduction, except that no potassium hydroxide was used. The oxo compound (8) was heated to 180°C with hydrazine hydrate and diethylene glycol for four hours. After cooling, the mixture was poured into water/brine and extracted with ethyl acetate. The reaction method worked extremely well and removal of the solvent afforded pure 5H-indeno[1,2-b]pyridine (4) in 89% yield.

Of the reduction methods investigated, that of DuPriest et al[24] gave superior results and was therefore used for further preparation of 5H-indeno[1,2-b]pyridine (4).

Reaction with Grignard reagents.

The addition of Grignard reagents to ketones afford tertiary alcohols. All the normal precautions associated with the Grignard reaction were taken.

The Grignard reaction between propylmagnesium bromide and the ketone (8) should produce 5-hydroxy-5-propyl-indeno[1,2-b]pyridine (218) according to the following reaction scheme.Scheme 149.



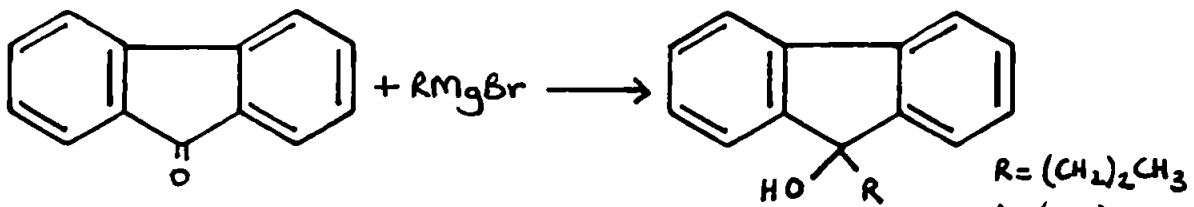
(8) (218)

Scheme 149

Attempts to produce (218) however,failed despite several attempts.

After each experiment, between 50 and 70% of the starting ketone (8) was recovered.

In an attempt to determine the reasons for the failure,the above experiment was repeated using (216) in place of 5H-indeno[1,2-b]pyridin-5-one (8).The expected product, with propylmagnesium bromide, being 9-hydroxy-9-propyl-fluorene (219, R=$(CH_2)_2CH_3$).Scheme 150.



(8) (219)

Scheme 150

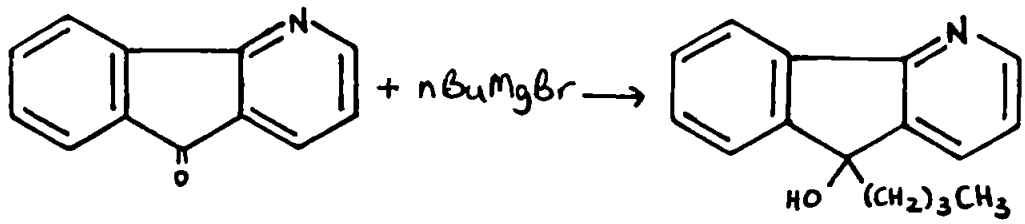
The reaction,however, afforded a yellow solid.T L C examination of the solid indicated two spots,very close together, Rf 0.32 and 0.29 (fluorenone).

Infrared examination of the solid indicated the presence of an alcohol, as well as the starting material.
Mass spectral examination of the solid indicated the presence of the desired alcohol (219, R=$(CH_2)_2CH_3$), (m/z 224 , appendix 1.32).
Repeated attempts to obtain the pure alcohol by flash chromatography (eluent 60% petroleum spirit (bp 40-60°)/ 40% ethanol) however, failed.

It appeared that the Grignard reaction was occurring , but not to completion. The above experiment was repeated but the solution was refluxed for 21 hours instead of 4 hours. T.L.C. examination of the crude product indicated five components including the starting material.
Repeated flash chromatography (80% petroleum spirit (bp 40-60°)/20% diethyl ether) gave a small amount of the desired alcohol (219, R=$(CH_2)_2CH_3$), with 60% of the starting ketone (216) being recovered. Mass spectrum (appendix 1.32)

When bromobutane was used to form the Grignard reagent, the resulting organomagnesium compound was reacted with fluorenone (216), a small amount of the desired alcohol, 9-butyl-9-hydroxyfluorene (219, R=$(CH_2)_3CH_3$) was obtained (2%), Appendix 1.32 . Scheme 150.

The Grignard reaction between butylmagnesium bromide and 5H-indeno[1,2-b]pyridin-5-one (8) afforded a sticky orange solid. Flash chromatography (elution with 55% petroleum spirit (bp 40-60)/45% ethyl acetate) gave a sample containing both the desired alcohol (220) and some starting material, as indicated by infrared examination (ν C=O 1715 cm^{-1}, ν OH 3306 cm^{-1}). Scheme 151.



(8) (220)

Scheme 151

Recrystallisation from ethanol gave the starting material (200mg).Rotor-evaporation of the filtrate gave a solid (70mg) containing the alcohol (220), contaminated with starting material (8), as indicated by the mass spectrum (appendix 1.33).

Attempts were made to separate the alcoholic product from the ketonic starting material using Girards-T reagent. Girards-T reagent (carbohydrazidomethylammonium chloride or trimethylaminoacetohydrazide chloride) (221) may be used to separate alcohols from ketones.

$$Cl^- \left\{ Me_3\overset{+}{N} \cdot CH_2 \cdot CONH \cdot NH_2 \right. \qquad (221)$$

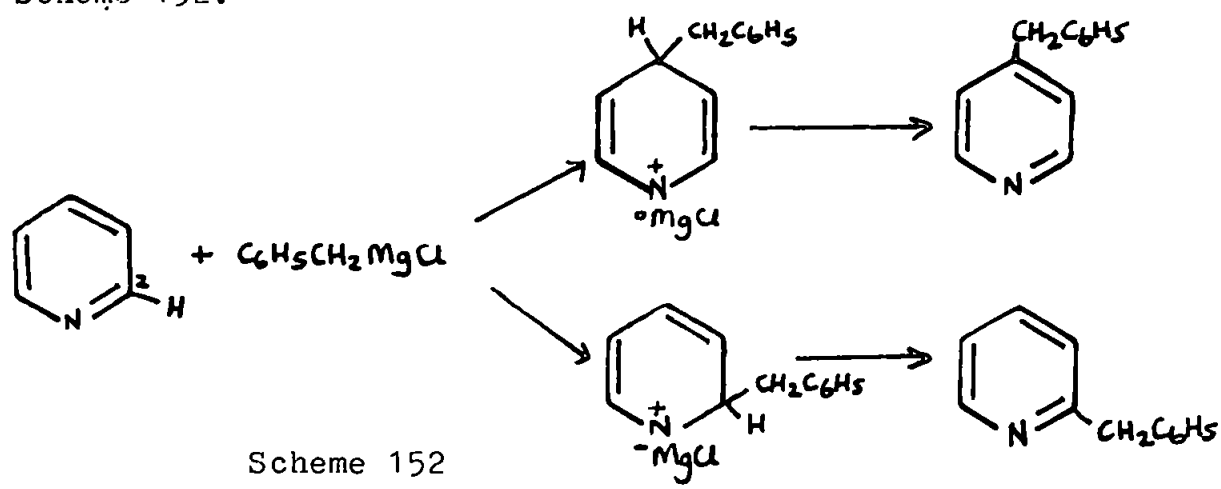
A trial run with fluorenone (216) and 9-hydroxyfluorene proved successful, the alcohol being obtained in 90% yield.

With 5H-indeno[1,2-b]pyridin-5-one (8) and 5-butyl-5-hydroxy-indeno[1,2-b]pyridine (220) however, the alcohol (220) was still contaminated with the ketone (8) and complete separation was not accomplished.

It may be possible that the Grignard reaction between fluorenone (209) and propylmagnesium bromide and butylmagnesium bromide does not occur readily because the alkylhalides are insufficiently reactive in this case. This may also be the case with the ketone (8).Here, the Grignard reagent is formed, as evidenced by the formation of a cloudy precipitate and the eventual disappearance of the magnesium turnings, but the desired alcohols (218 , 220) are not obtained in appreciable yields.

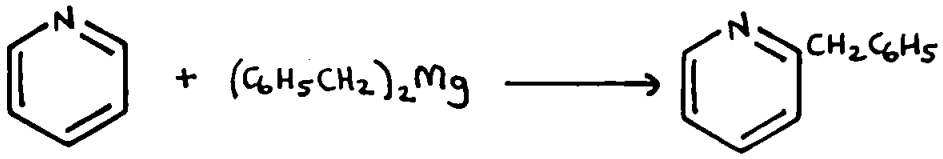
In the case of (8) it may be possible that a side-reaction was occurring between (8) and the Grignard reagent leading to alkylation of the ketone (8) as opposed to the expected alcohol formation.

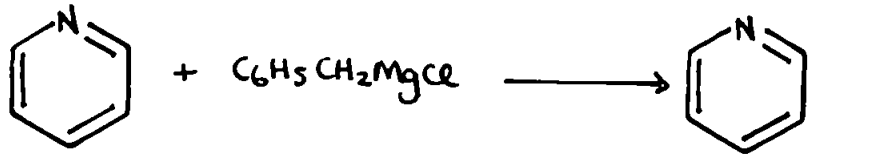
The alkylation of pyridines by addition of the Grignard reagent across the azomethine linkage has been reported[106]. -Scheme 152.



Scheme 152

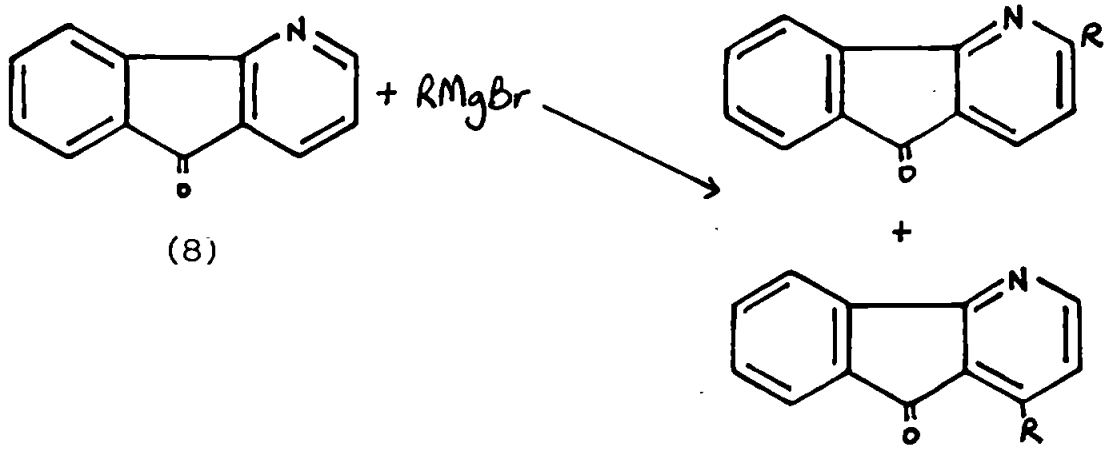
Bergmann and Rosenthal[107] have reported that pyridine and dibenzylmagnesium gave 2-benzylpyridine, while Veer and Goldschmidt[108] found that pyridine and benzylmagnesium chloride gave 4-benzylpyridine. Scheme 153.





Scheme 153

It may therefore be possible that the ketone (8) is being alkylated by addition of the Grignard reagent across the azomethine linkage giving the 2- or the 4-isomer.Scheme 154.

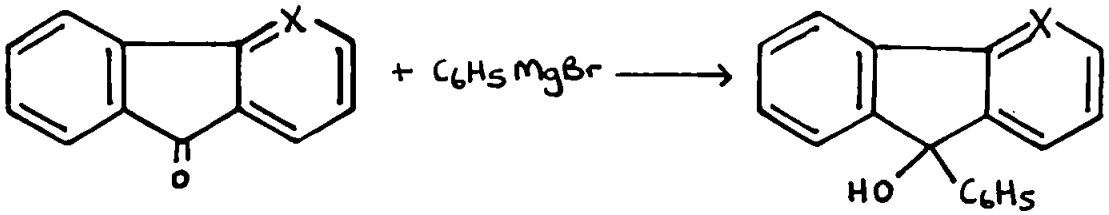


(8)

Scheme 154

However, on no occasion were the alkylated products indicated in scheme 154, observed by mass spectrometry or infrared spectroscopy.

Bromobenzene is known to be a reactive alkylhalide. Grignard reaction between phenylmagnesium bromide and both 5H-indeno [1,2-b] pyridin-5-one (8) and fluorenone (216) proved successful. Scheme 155.



X=N (8)

X=C (216)

X=N (222)

X=C (223)

Scheme 155

Starting from (8), 5-hydroxy-5-phenylindeno[1,2-b]-pyridine (222) was obtained in 53% yield.(Appendix 1.35). When diethyl ether was used as solvent and reaction proceeded for four hours, the alcohol (222) was obtained in 35% yield. When refluxing was increased to 10 hours, the yield of the alcohol (222) was increased to 53%. Use of T H F as an alternative solvent afforded the alcohol (222) in 50% yield.

In all cases the alcohol (222) was obtained by Flash chromatography, using 50% petroleum spirit (bp 40-60)/ 50% ethyl acetate as eluent.

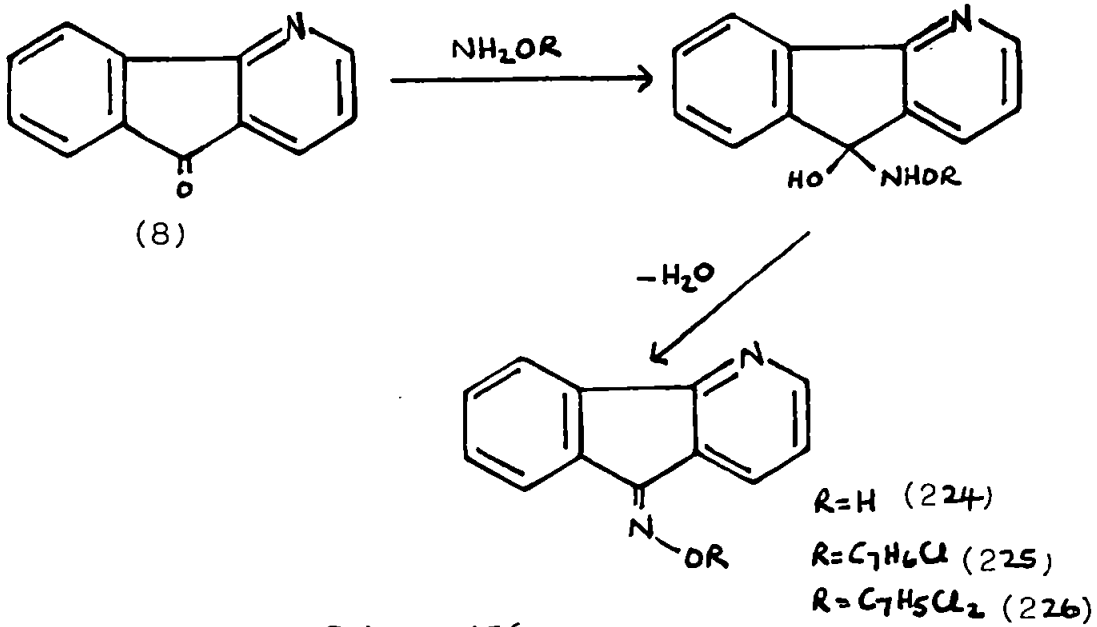
From fluorenone (216), 9-hydroxy-9-phenylfluorene (223) was obtained in 15% yield when diethyl ether was used as solvent.

Changing the solvent to T H F increased the yield to 57%.

Oxime formation

Following a general textbook method[109], the oxime of 5H-indeno[1,2-b]pyridin-5-one (8), (224) was obtained in good yield (63%). Scheme 156.

The reaction proceeds by the addition of the nitrogen nucleophile, followed by the elimination of water. In general the reaction proceeds as indicated in Scheme 156.



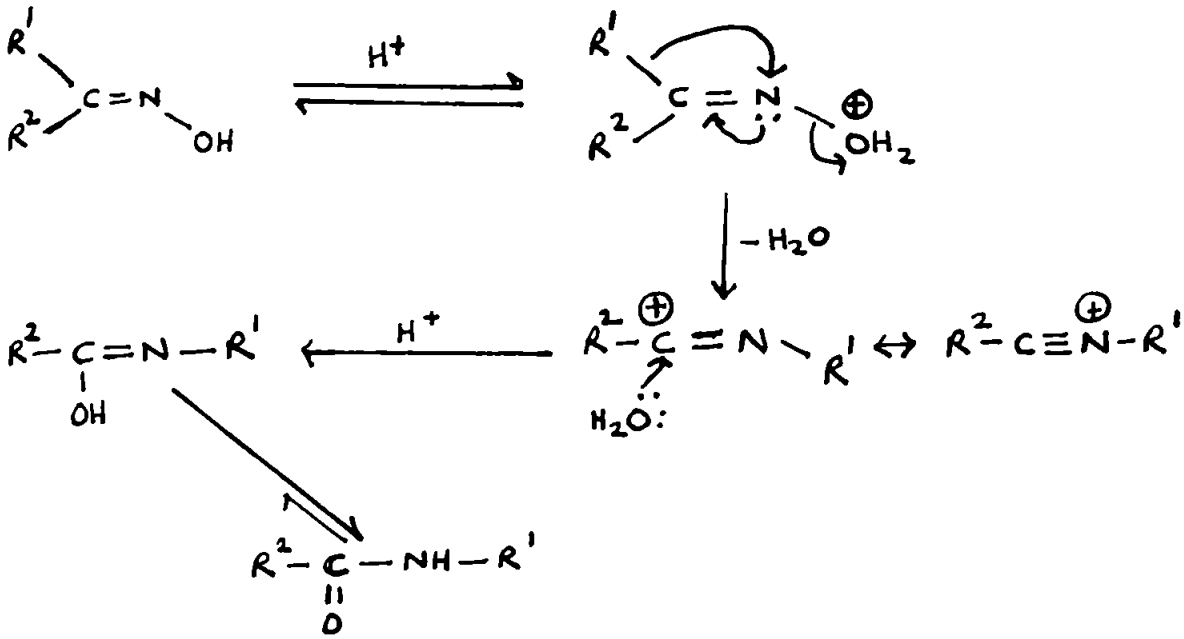
(8)

Scheme 156

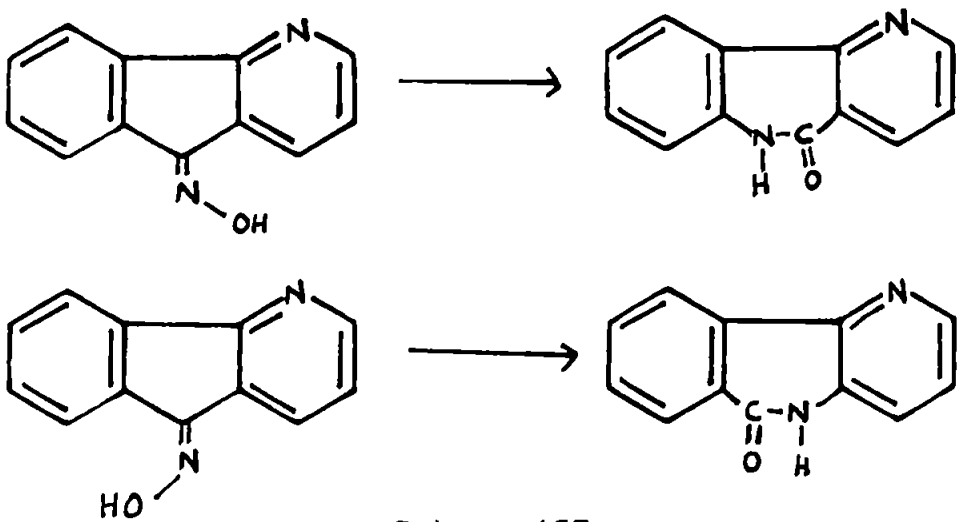
Key Organics (Camelford) provided two substituted hydroxylamines which were used following the general method to afford the two substituted oximes - 5H-indeno[1,2-b]-pyridin-5-one 4-chlorobenzyloxime (225) and 5H-indeno-[1,2-b]pyridin-5-one 2,4-dichlorobenzyloxime (226) in good yields, 68% and 91% respectively.

The stereochemistry of the oxime is not known, but can be found by analysis of the amide formed on the Beckmann rearrangement of the oxime.

Under acidic conditions, oximes undergo rearrangement to give substituted amides thus:



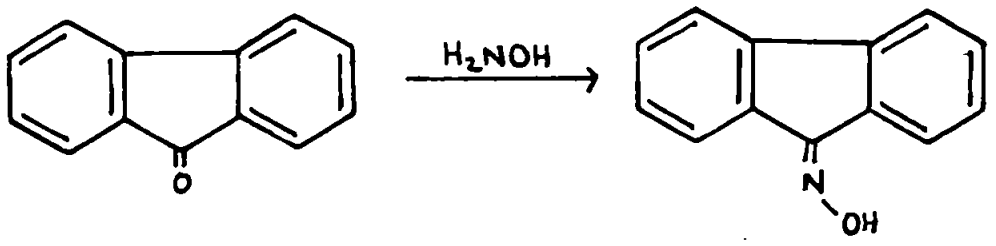
The reaction involves migration of an alkyl group to the electron deficient center.It is the alkyl group trans- to the hydroxyl group of the oxime which migrates. The possible products from 5H-indeno[1,2-b]pyridine-5-one oxime (224) by the Beckmann rearrangement would be as shown in Scheme 157.



Scheme 157

In order to optimise the reaction conditions for the Beckmann rearrangement, the model compound 9-fluorenone (216) was used.

9-Fluorenone oxime (227) was prepared in good yield (84%).Scheme 158.

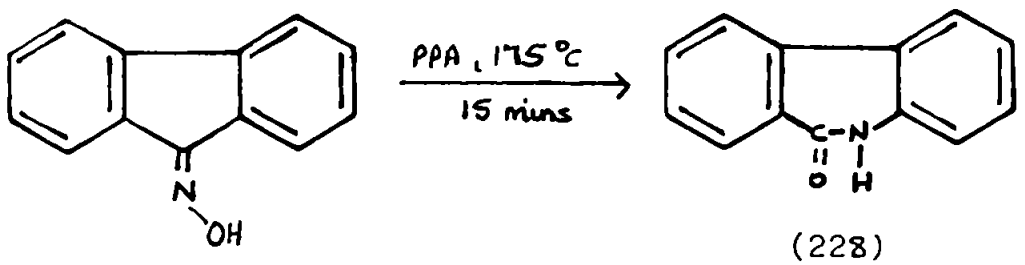


(216) (227)

Scheme 158

The Beckmann rearrangement was carried out according to the method of Vogel[103].

The oxime (227) was heated, with stirring , at 175°C in polyphosphoric acid for 15 minutes. The reaction mixture was cooled and stirred into cold water.The solid that separated out was identified as the known compound , 6-phenanthridone (228), using mass spectrometry, infrared spectroscopy and melting point. Scheme 159.



(227) (228)

Scheme 159

Attempts to rearrange 5H-indeno[1,2-b]pyridine-5-one oxime (224) under similar conditions, to give the desired amide, proved unsuccessful.

Initially, using the method of Vogel[103], the oxime (224) was added to polyphosphoric acid and the mixture was heated on a water bath. The mixture was poured immediately onto crushed ice and stirred.

As no precipitate appeared NaOH was added to pH 7 to yield a white precipitate which was collected and dried.

The suspected amide was then characterised.The yield was high as was the melting point (too high to be determined by 'electrothermal' equipment). The infrared spectrum indicated the presence of a carbonyl group at 1636cm^{-1} and a N-H stretching at 3200cm^{-1}.

The mass spectrum had a molecular ion of 196, as expected, the fragmentation pattern , however , did not correspond to the expected amide product.(appendix I.41)

It was difficult to show whether the solid was homogeneous or not because the solid product did not dissolve in most known solvents.

Alternative methods for the Beckmann rearrangement of the oxime (224) were then investigated.

The experiment was repeated at higher temperatures of 120°C and 180°C, and in both cases, approximately 60% of the starting oxime was recovered.

The attempted rearrangement was repeated at 120°C for extended periods of time (30 minutes and 1 hour.)

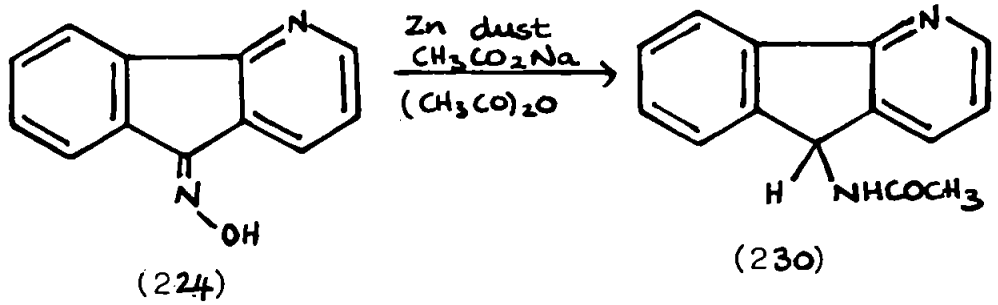
Again,only starting oxime was recovered in 70% yield.

Note.Compound (229) is not referred to in this thesis.

Miscellaneous reactions.

Reduction of the oxime (224)

The oxime (224), when treated with zinc dust, acetic anhydride and sodium acetate[28], was reduced to afford the acetamido compound (230) in 64% yield.Scheme 160.



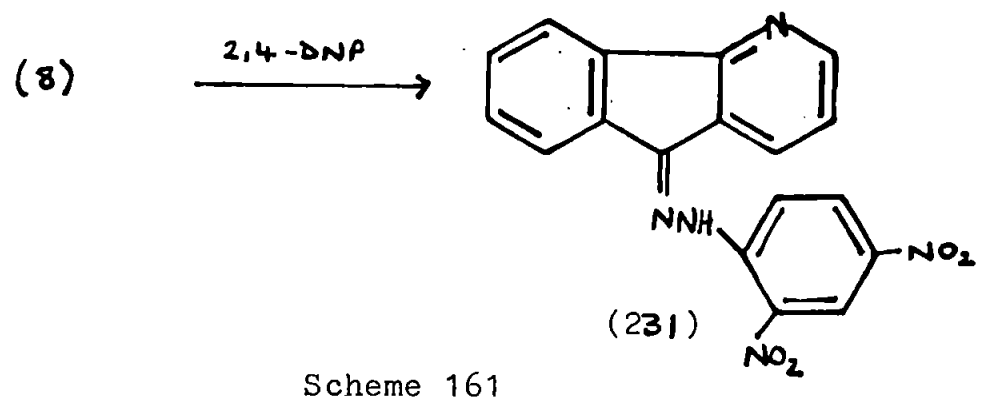
(224) (230)

Scheme 160

Reaction with 2,4-dinitrophenylhydrazine.

There are several derivatives which maybe prepared from ketones (they are usually used as 'spot' tests for the presence of carbonyl compounds. One such derivative is the 2,4-dinitrophenylhydrazone.

When 5H-indeno[1,2-b]pyridin-5-one (8) was added to a solution of 2,4-dinitrophenylhydrazine in methanol, the bright orange precipitate of the hydrazone (231) separated out.Scheme 161.



(231)

Scheme 161

Electrophilic Aromatic Substitution studies on 5H-indeno[1,2-b]pyridin-5-one (8) and 5H-indeno[1,2-b]pyridine (4).

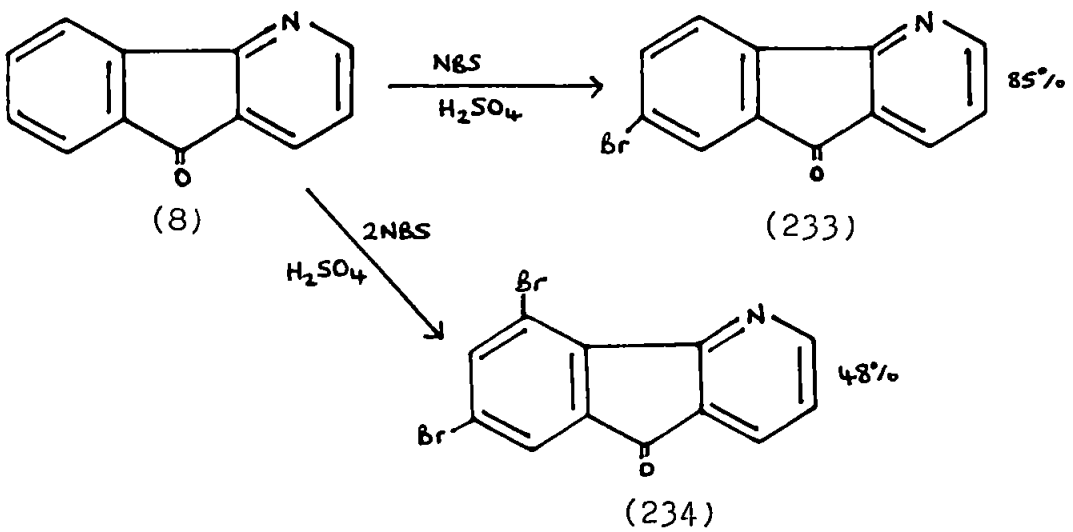
Several workers have prepared nitro- and bromo- derivatives of (8) and (4). In all cases reported, the substituent enters at the 7-position[12,13,14,15].

Bromination.

As previously reported (Chapter 3, page 8), Mlochowski and Szulc[15] have prepared several bromo- derivatives of 5H-indeno[1,2-b]pyridin-5-one (8).

These compounds were prepared according to the literature method. 7-bromo-5H-indeno[1,2-b]pyridin-5-one (233) was prepared in 85% yield by the reaction of the oxo compound (8) with N-Bromosuccinamide (NBS) in a 1:1 ratio.

When 2 equivalents of NBS were used, the dibromo compound, 7,9-dibromo-5H-indeno[1,2-b]pyridin-5-one (234) was obtained in 48% yield. Scheme 162.



Scheme 162

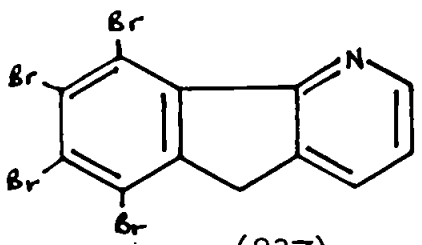
Attempts were then made to prepare bromides of 5H-indeno[1,2-b]pyridine (4)

Treating (4) with NBS in a 1:1 ratio did not afford the expected monobromo compound ; instead a dibromo-compound (235) was obtained , as indicated by mass spectrometry (appendix I.44, m/z 323).

When two equivalents of NBS were used, a tribromo-compound (236) and not the expected dibromo- compound (235) was obtained , as evidenced by mass spectrometry (appendix I.45 , m/z 401).

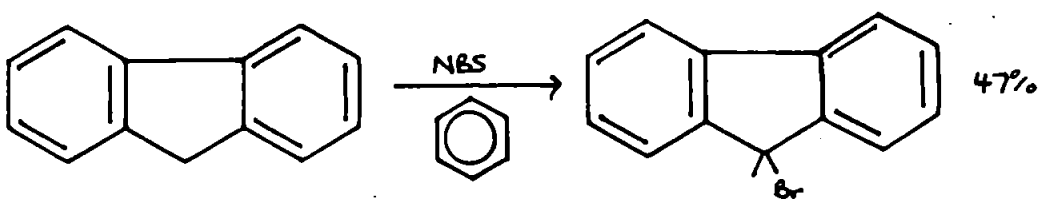
The reaction of 5H-indeno[1,2-b]pyridine (4) with a 3.5 excess of NBS afforded a tetrabromo- compound (237).

Each of these compounds (235,236 and 237) are new.



(237)

Although it is known that the bromine atom enters the C-7 with 5H-indeno[1,2-b]pyridin-5-one (8), it may be possible that with 5H-indeno[1,2-b]pyridine (4), substitution may also occur at C-5 , as in fluorene substitution with bromine occurs in the C-9 position.Scheme 163.

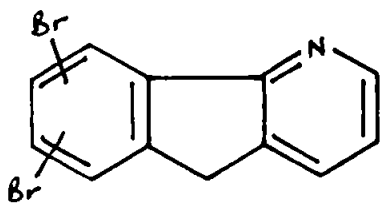


Scheme 163

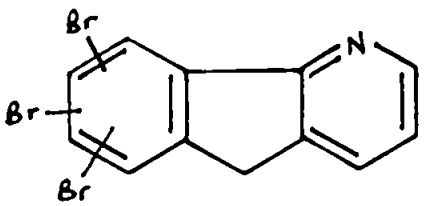
^{1}H NMR study of the tetrabromo- compound (237), however, indicates the presence of methylene protons at 3.8 ppm (appendix II.16).^{13}C NMR also indicates the presence of $-CH_2-$ at 37 ppm (appendix III.13).A DEPT measurement of (237) indicates the presence of $-CH_2-$ at 37 ppm at -ve intensity of 75.52% .(appendix III.14).

It appears therefore that bromination of (4) occurs solely in the benzene ring, and that the structure given above for (237) is correct.

It is reasonable to assume therefore, that compounds (235) and (236) have the structures indicated below :



(235)



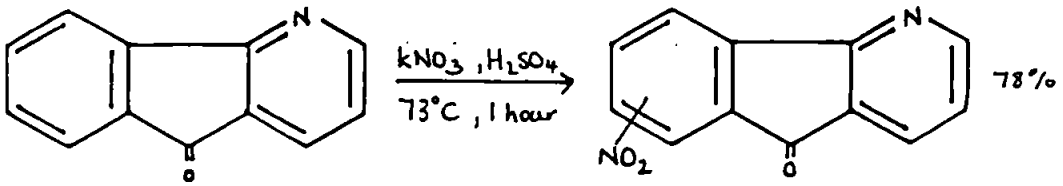
(236)

The dibromo- and tribromo- compounds (235 and 236 respectively) could not , however, be obtained in a pure form, and no data could be collected for these compounds.

The tetrabromo- compound was obtained in good yield (62%).

Nitration.

Nitration of the oxo compound (8) using the method of Petrow [12] gave a nitro- compound (238) in 78% yield, as confirmed by mass spectrometry (appendix I.47) and ^{13}C NMR spectroscopy (appendix III.15). Scheme 164.

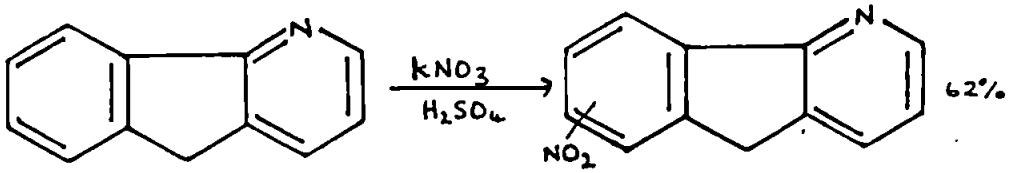


(8) (238)

Scheme 164

It is known that on nitration of 9H-indeno[2,1-c]pyridin-9-one (12), the nitro- group enters at the C-7 position ; also bromination of 5H-indeno[1,2-b]pyridin-5-one (8) is known to occur in the C-7 position. The nitro- group in (238) was tentatively assigned to C-7 and the compound obtained (238) is thought to be 7-nitro-5H-indeno[1,2-b]-pyridin-5-one .

Nitration of 5H-indeno[1,2-b]pyridine (4), again using the method of Petrow[12] , afforded a nitro- compound, thought to be 7-nitro-5H-indeno[1,2-b] pyridine (239) in 62% yield, as confirmed by mass spectrometry (appendix I.48) and ^{1}H NMR spectroscopy (appendix II.18).Scheme 165 .

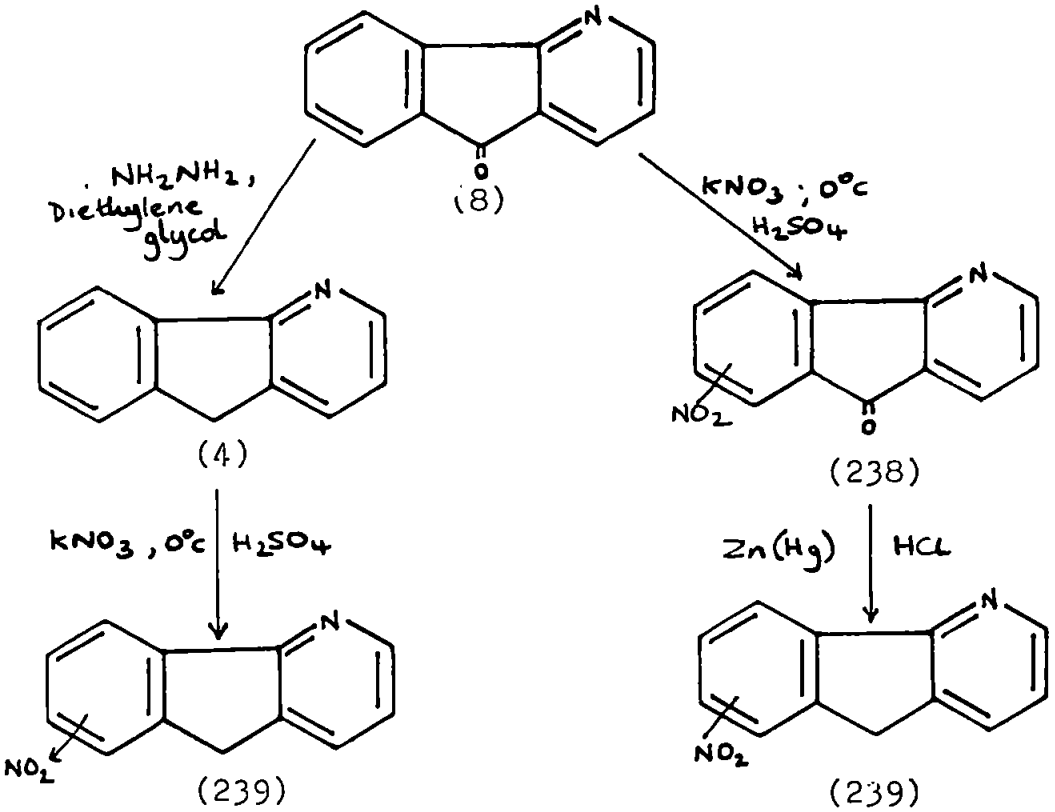


(4) (239)

Scheme 165

^{13}C nmr (appendix III.16) , however, indicates the presence of three compounds (nitro isomers) with CH_2 resonances appearing at **34.8** , **34.7** and 34.5 ppm.It may be possible that nitration occurs in the C-6 and C-9 position as well as the expected C-7 position to give the three nitro-isomers that are seen.

To prove that substitution of the nitro- group occurs at the same position in both the 5H-indeno[1,2-b]pyridin-5-one (8) and 5H-indeno[1,2-b]pyridine (4), the following reaction scheme was carried out.Scheme 166.



Scheme 166

Route 1. The ketone (8) was reduced using the method of DuPriest [24] to afford 5H-indeno[1,2-b]pyridine (4) in 89% yield.Nitration of (4) occurred in 62% yield giving (239).

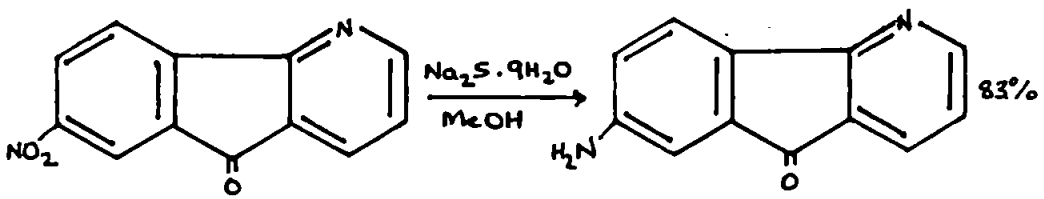
Route 2. The nitration of (8) occurred in good yield (78%) to give (238).Attempts were then made to reduce the carbonyl function of (238) to afford the nitro compound (239).

The method of DuPriest [24] was used to attempt to reduce the nitro ketone (238).However, although a product was obtained it proved not to be the desired nitro- compound (239).

From spectroscopic evidence, it appears that both functional groups were reduced and that an amine - assumed to be 7-amino-5H-indeno[1,2-b]pyridine (240) was obtained in good yield (69%), as confimed by mass spectroscopy (appendix I.49) and ^{1}H NMR spectroscopy (appendix II.19)

However, Clemmensen reduction [103] of the nitro compound (238), did afford the desired reduced nitro- compound (239) in 35% yield.The physical properties obtained for this compound (infrared and mass spectroscopy,TLC and m.p.) were identical to those obtained for the compound obtained by the direct nitration of the oxo compound (8), thus confirming that nitration of (8) and (4) occurs in the same position, assumed to be the C-7 position.

The nitro- group provides a useful route to a variety of other derivatives using standard synthetic reactions. Using a standard procedure for the reduction of nitro compounds in Vogel [103], the nitro compound (238) was reduced to the amine 7-amino-5H-indeno[1,2-b]pyridin-5-one (241)- in 83% yield, by treatment of (238) with sodium sulphide in a solution of methanol.Scheme167.

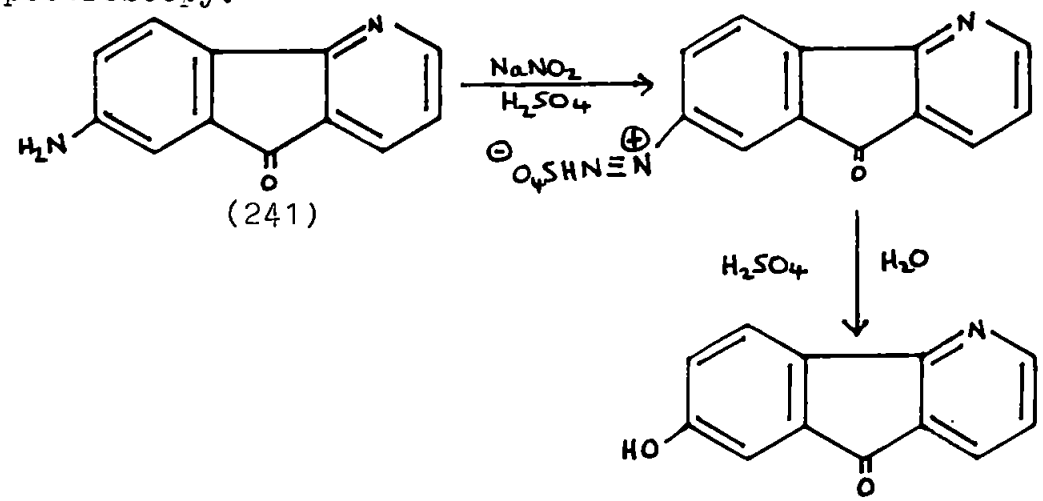


(238) (241)

Scheme 167

As previously mentioned, 7-amino-5H-indeno[1,2-b]pyridine (240) was also unexpectedly obtained , using the method of DuPriest[24], by reduction of 7-nitro-5H-indeno[1,2-b]pyridin-5-one (238) in diethylene glycol with hydrazine hydrate.

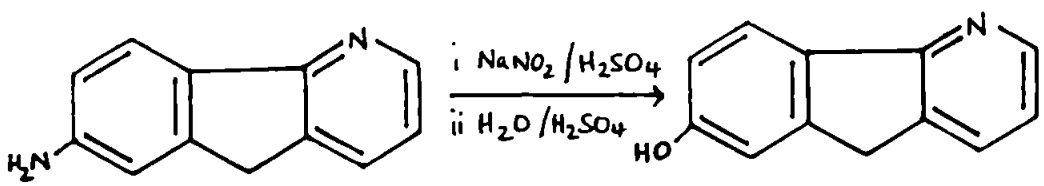
The amine group of (241) was then diazotised and reacted with boiling water to afford the phenol (242) according to the following reaction scheme, Scheme 168, confirmed by mass (appendix I.51) and ^{1}H NMR (appendix II.21) spectroscopy.



(241) (242)

Scheme 168

Under similar reaction conditions, diazotisation of (240) followed by refluxing the diazonium salt with boiling water afforded the phenol 7-hydroxy-5H-indeno[1,2-b]pyridine (243), as confirmed by mass spectrometry (appendix I.52) and ^{1}H NMR spectroscopy (appendix II.22).Scheme 169.



(240) (243)

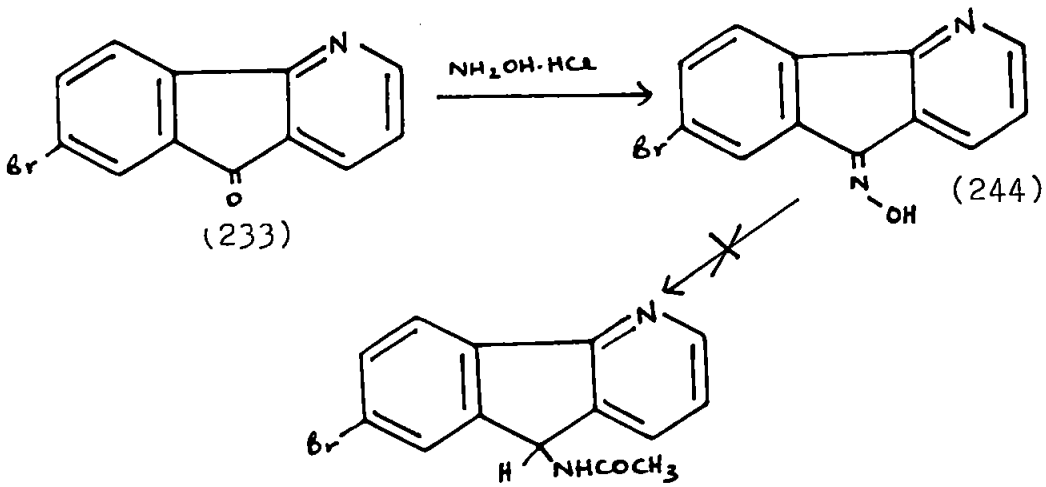
Scheme 169

Reactions of 7-bromo-5H-indeno[1,2-b]pyridine-5-one (233) and 7-nitro-5H-indeno[1,2-b]pyridine-5-one (238).

The oxime preparation and subsequent reduction[28], as described for the oxime (224),page 136, was repeated for 7-bromo- (233) and 7-nitro-5H-indeno[1,2-b]pyridine-5-one (238).

Reaction of (233) with hydroxylamine hydrochloride afforded the oxime (244) in 85% yield[109].

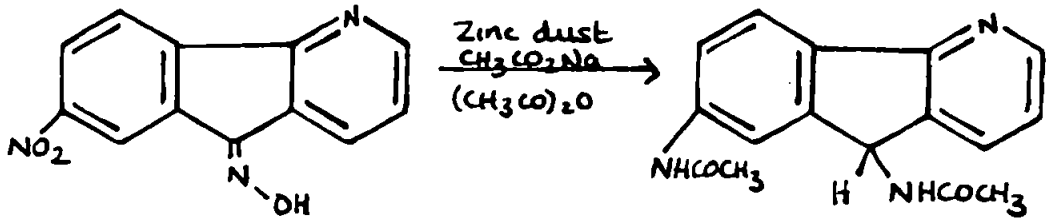
Attempts to convert the oxime (244) to the acetamido derivative using the method of Feitelson and Petrow[28],however failed.Scheme 170 .



Scheme 170

The reaction of 7-nitro-5H-indeno[1,2-b]pyridin-5-one (238) with hydroxylamine hydrochloride afforded the desired oxime (245) in 99% yield.[109]

Reaction with zinc dust,acetic anhydride and sodium acetate[28] afforded an unexpected di-acetamido compound (246) in 94% yield, as indicated by infrared and mass spectrometry (appendix I.57). The spectra also confirmed the absence of the nitro- group.Scheme 171 .



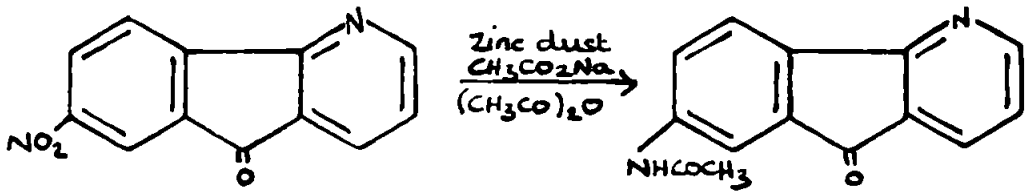
(245) (246)

Scheme 171

It appears that the reaction conditions used also reduced the nitro- group to the amino group, which was then acetylated to the acetamido group.

$$-NO_2 \longrightarrow -NH_2 \longrightarrow -NHCOCH_3$$

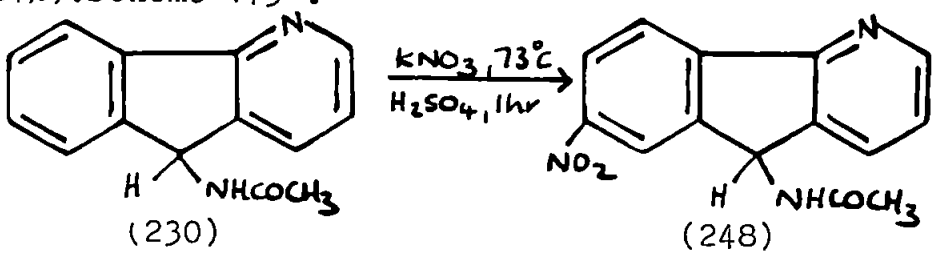
This was confirmed by reacting 7-nitro-5H-indeno[1,2-b]-pyridin-5-one (238) with acetic anhydride, zinc dust and sodium acetate.[28] As expected , 7-acetamido-5H-indeno[1,2-b]-pyridin-5-one (247) was obtained ,albeit in poor yield (12%). Scheme 172 .



(238) (247)

Scheme 172

5-Acetamido-7-nitro-5H-indeno[1,2-b]pyridine (248) was eventually prepared by nitration of 5-acetamido-5H-indeno-[1,2-b]pyridine (230), when (248) was obtained in good yield (87%).[13] Scheme 173 .



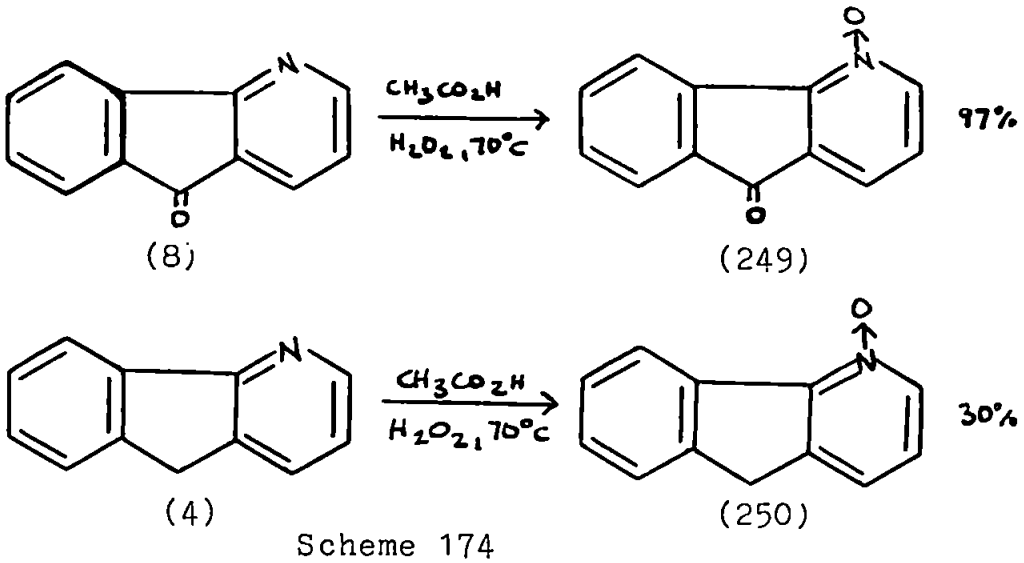
(230) (248)

Scheme 173

Reactions involving the Heterocyclic ring.

N-oxide formation.

The N-oxides of 5H-indeno[1,2-b]pyridin-5-one (8) and 5H-indeno[1,2-b]pyridine (4) were prepared using the method of Ochiai[110], which involves heating the appropriate indenopyridine with acetic acid and hydrogen peroxide at 70°C for approximately 18 hours. Although the derivative of the ketone (249) was obtained in good yield (75%), the pyridine (4) gave only a poor yield (30%) of the N-oxide (250). Scheme 174.

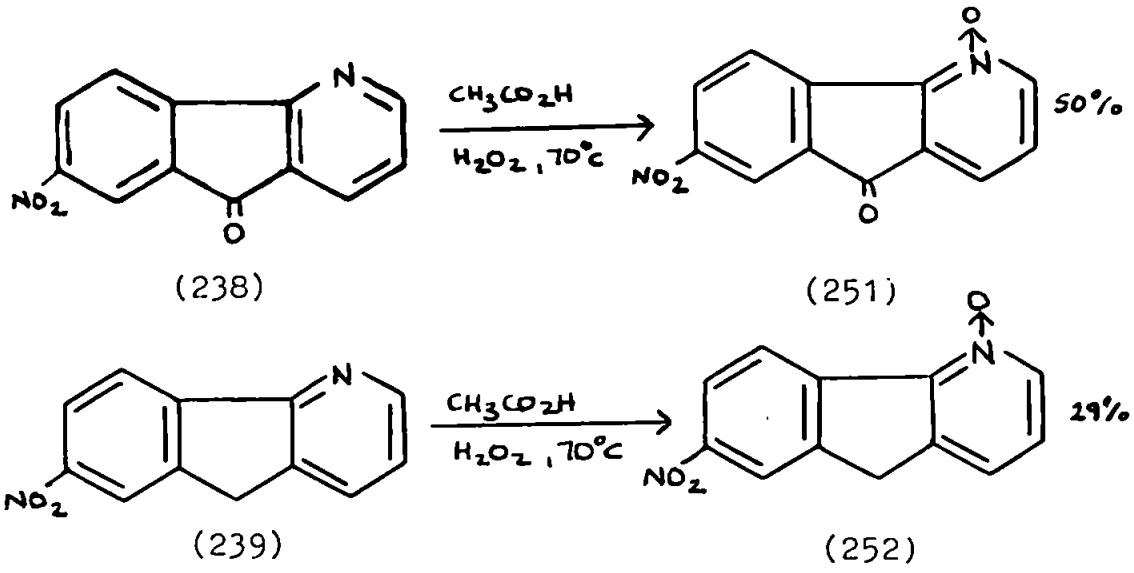


(8) (249)

(4) (250)

Scheme 174

Similarly, the N-oxides of 7-nitro-5H-indeno[1,2-b]pyridin-5-one (251) and 7-nitro-5H-indeno[1,2-b]pyridine (252) were prepared, using the above method[110], in 50% and 29% yield respectively, starting from (238) and (239) respectively. Scheme 175.



Scheme 175

Summary.

From 3-methyl-2-phenylpyridine (158), the ketone 5H-indeno[1,2-b]pyridine-5-one (8) was made. Reduction of (8) afforded the methylene compound- 5H-indeno[1,2-b]-pyridine (4).

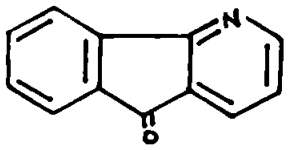
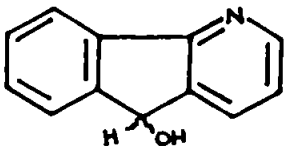
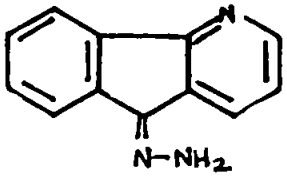
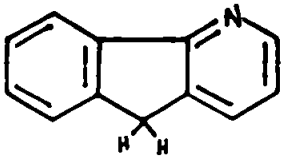
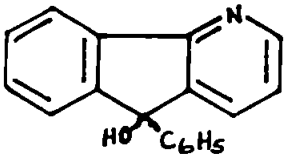
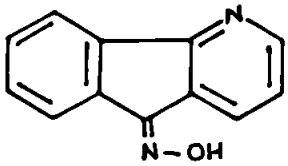
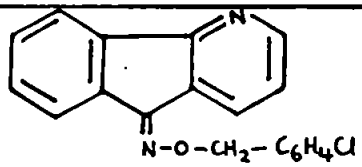
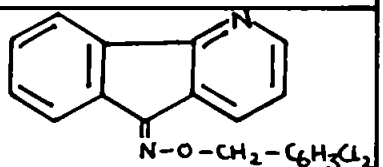
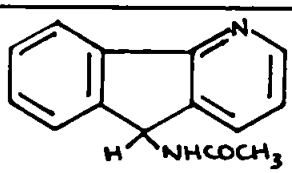
Using (8) and (4) as starting materials, both known and novel indenopyridines were made using classical chemical reactions, such as the Grignard reaction, oxime preparation, electrophilic aromatic substitution and nucleophilic substitution in the heterocyclic ring.

Using these methods 22 novel compounds were synthesised.

A summary of the known and novel indenopyridines synthesized from 3-methyl-2-phenylpyridine (158) are shown in Table 3, together with their structural formula and relative molecular weight, (pages 151a-d).

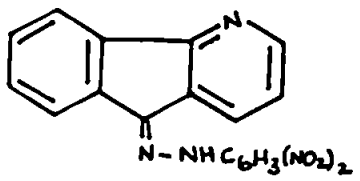
Table 4 is a summary of the other compounds produced from this chapter, together with their structural formula and relative molecular weight, (page 151e)

Table 3. Summary of the novel and known indenopyridines synthesized from 3-methyl-2-phenylpyridine.

5H-Indeno[1,2-b]pyridin-5-one $C_{12}H_7NO_2$ RMW 181 Known	
5-Hydroxy-5H-indeno[1,2-b]pyridine $C_{12}H_9NO$ RMW 183 Known	
5H-Indeno[1,2-b]pyridine-5-one hydrazone $C_{12}H_9N_3$ RMW 195 Known	
5H-Indeno[1,2-b]pyridine $C_{12}H_9NO$ RMW 167 Known	
5-Hydroxy-5-phenylindeno[1,2-b]pyridine $C_{18}H_{13}NO$ RMW 259	
5H-Indeno[1,2-b]pyridine-5-one oxime $C_{12}H_8N_2O$ RMW 196 Known	
5H-Indeno[1,2-b]pyridine-5-one 4-chlorobenzyloxime $C_{19}H_{13}N_2OCl$ RMW 320	
5H-Indeno[1,2-b]pyridine-5-one 2,4-dichlorobenzyloxime $C_{19}H_{12}N_2OCl_2$ RMW 354	
5-Acetamido-5H-indeno[1,2-b]pyridine $C_{14}H_{12}N_2O$ RMW 224	

5H-Indeno[1,2-b]pyridin-5-one 2,4-dinitrophenylhydrazone

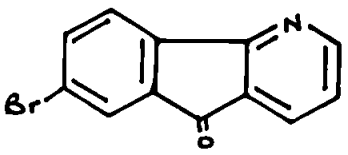
$C_{18}H_{11}N_5O_4$ RMW 361



7-Bromo-5H-indeno[1,2-b]pyridin-5-one

$C_{12}H_6NOBr$ RMW 259

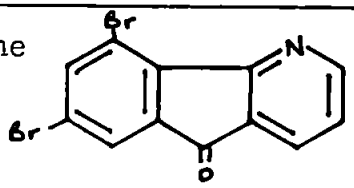
Known



7,9-Dibromo-5H-indeno[1,2-b]pyridin-5-one

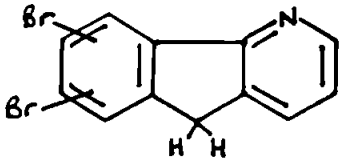
$C_{12}H_5NOBr_2$ RMW 337

Known



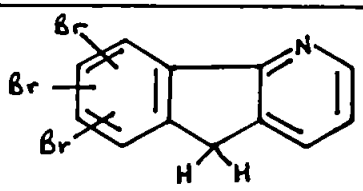
Dibromo-5H-indeno[1,2-b]pyridine

$C_{12}H_7NBr_2$ RMW 323



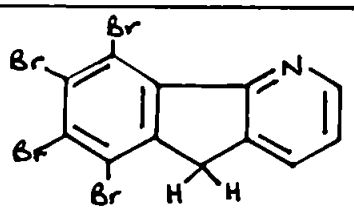
Tribromo-5H-indeno[1,2-b]pyridine

$C_{12}H_6NBr_3$ RMW 401



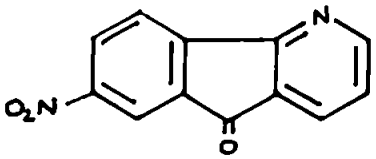
6,7,8,9-tetrabromo-5H-indeno[1,2-b]pyridine

$C_{12}H_5NBr_4$ RMW 479



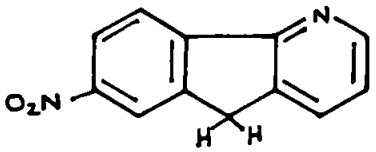
7-Nitro-5H-indeno[1,2-b]pyridin-5-one

$C_{12}H_6N_2O_3$ RMW 226



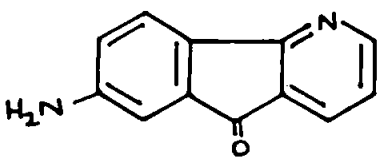
7-Nitro-5H-indeno[1,2-b]pyridine

$C_{12}H_8N_2O_2$ RMW 212



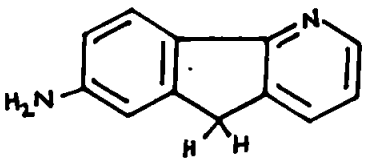
7-Amino-5H-indeno[1,2-b]pyridin-5-one

$C_{12}H_8N_2O$ RMW 196



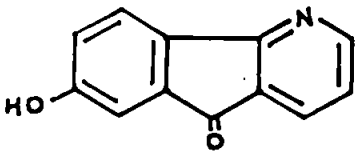
7-Amino-5H-indeno [1,2-b] pyridine

$C_{12}H_{10}N_2$ RMW 182



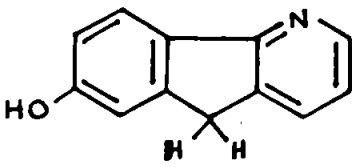
7-Hydroxy-5H-indeno [1,2-b] pyridin-5-one

$C_{12}H_7N_2O$ RMW 197



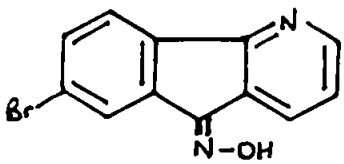
7-Hydroxy-5H-indeno [1,2-b] pyridine

$C_{12}H_9NO$ RMW 183



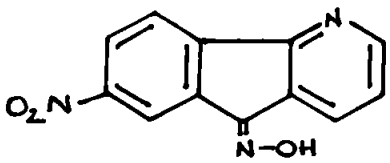
7-Bromo-5H-indeno [1,2-b] pyridin-5-one oxime

$C_{12}H_7N_2OBr$ RMW 274



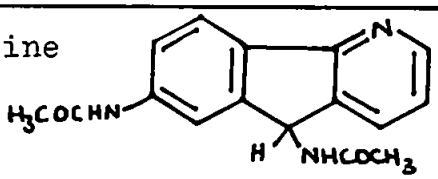
7-Nitro-5H-indeno [1,2-b] pyridin-5-one oxime

$C_{12}H_7N_3O_3$ RMW 241



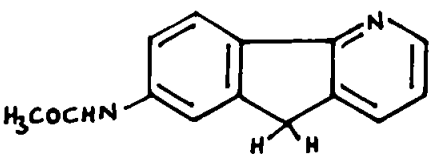
5,7-Diacetamido-5H-indeno [1,2-b] pyridine

$C_{16}H_{15}N_3O_2$ RMW 281



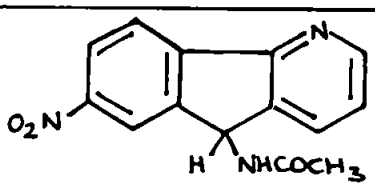
7-Acetamido-5H-indeno [1,2-b] pyridine

$C_{14}H_{12}N_2O$ RMW 224



5-Acetamido-7-nitro-5H-indeno [1,2-b] -pyridine

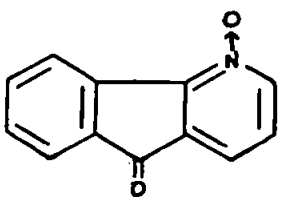
$C_{14}H_{11}N_3O_3$ RMW269



5H-Indeno [1,2-b] pyridin-5-one N-oxide

$C_{12}H_7NO_2$ RMW 197

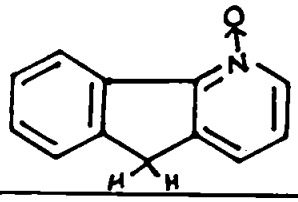
Known



5H-indeno[1,2-b]pyridine N-oxide

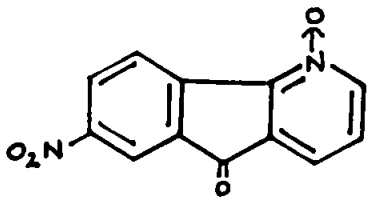
$C_{12}H_9NO$ RMW 183

Known



7-Nitro-5H-indeno[1,2-b]pyridin-5-one N-oxide

$C_{12}H_6N_2O_4$ RMW 242



7-Nitro-5H-indeno[1,2-b]pyridine N-oxide

$C_{12}H_8N_2O_3$ RMW 228

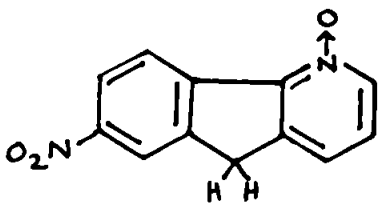
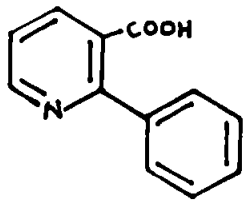
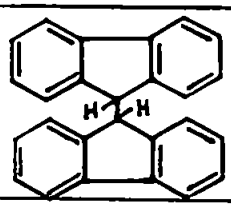
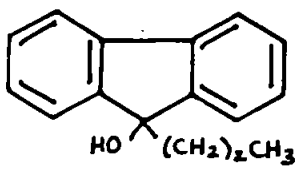
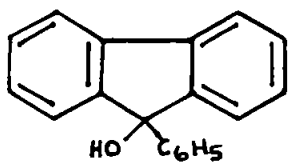
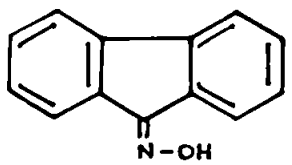
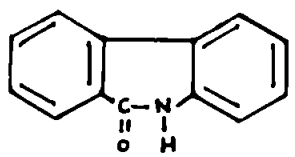


Table 4. Summary of other compounds produced from Chapter 8.

2-Phenyl-3-pyridine carboxylic acid $C_{12}H_9NO$ RMM 199	
9,9'-Bifluorenyl $C_{26}H_{18}$ RMM 330	
9-Hydroxy-9-propylfluorene $C_{16}H_{16}O$ RMM 224 New	
9-hydroxy-9-phenylfluorene $C_{19}H_{14}O$ RMM 258	
Fluorenone oxime $C_{13}H_9NO$ RMM 195	
Phenanthridone $C_{13}H_9NO$ RMM 195	

Conclusions and Further Work.

Attempts to make indenopyridines by the Vilsmeier-Haack formylation of enamidoindenes proved not to be viable due to the formation, under acidic conditions, of di-condensation products. Omission of the acid catalyst resulted in the formation of 2-acetamidoindene (183) in variable yields. 1-Acetamidoindene (182) could not be prepared.

It also seemed that 2-acetamidoindene (183) was made via an impurity in commercial 2-indanone (168). As no reaction occurred when pure 2-indanone (168) was used, this work was discontinued. Further work, however, is obviously needed on these reactions. If the enamidoindenes could be made in good yield, the Vilsmeier-Haack formylation could be used as a potential route to Indenopyridines.

Investigations of the Wolff rearrangement of benz[h]quinoline-5,6-diazoketone(186) also proved to be unsuccessful. Although 9H-fluorene-9N-tertbutylcarboxamide (197)was obtained by rearrangement of 9-diazo-10-phenanthrone (195), rearrangement of the nitrogen analogue was not achieved. Spectroscopic data indicated the presence of the desired indenopyridine, purification , however, could not provide pure samples.

Further work could involve the addition of a tertiary amine to the methanol/tetrahydrofuran system to see if rearrangement could be encouraged. Work could also be carried out into investigating the use of different solvent systems to see if this could effect rearrangement.

Using a published synthesis, a range of indenopyridines were made from 3-methyl-2-phenylpyridine (79).

Further work could include investigations into the following areas:

1 the reaction between Grignard reagents and 5H-indeno[1,2-b]-pyridine-5-one (8).

2 substitution reactions of the N-oxides of 5H-indeno[1,2-b]-pyridine (4) and 5H-indeno[1,2-b]pyridine-5-one (8) and

3 nucleophilic substitution in the heterocyclic ring of the indenopyridines, for example, the Chichibabin reaction.

Experimental

General , Solvents and Reagents.

Common solvents and reagents, obtained from commercial sources, were used as received unless otherwise stated. Any chemicals which were required to be anhydrous or of high purity, were prepared using the methods described by Perrin[111] et al and Keese[112] et al.

Distilled water was used throughout.

Solvents were evaporated under reduced pressure using a 'Buchi' rotary evaporator.

Melting points (mp) were determined in capillary tubes using an 'Electro-thermal' apparatus, and quoted values are uncorrected.

Chromatographic procedures

The purity of most products was checked by Thin Layer Chromatography, using the ascending technique on 0.25mm layers of silica gel (Kiselgel G.F. 254).All T L C plates were pre-eluted with ethyl acetate , and developed with 50:50 petroleum spirit (bp 40-60°C) and ethyl acetate, unless otherwise stated.

Components were visualised under a UV lamp at 254 nm.

Spectroscopic Procedures

Infrared Spectroscopy

Spectra were recorded using a grating spectrophotometer (Perkin-Elmer model 1330), from a potssium bromide disc.

Mass Spectrometry (MS)

Mass spectra were obtained on a Kratos 25 computerised mass spectrometer, using 'probe' samples. Typical conditions were:

Scan rate ca. every ½ second from 50-500	
Filament current	5.0 A
Emission current	700 uA
Electron voltage	40 eV

The following temperature programme was normally used. At scan 20 the air was turned off; the temperature was increased to 60°C at scan 40 and then by 20°C every 20 scans until the maximum temperature was reached (250°C). All computations were carried out on a Data General desktop computer using a Tektronix 4105 monitor system with a Tektronix 4695 printout. Kratos DS 55 and DS 90 software packages were used for acqusition and processing repectively.

Winchester discs were used for temporary storage, and tapes for long storage.

Photolysis apparatus.

Photolysis was carried out using an immersion well photochemical reactor, which allows solutions of reactants to be irradiated by ultraviolet or visible radiation produced by a lamp located in a cooled, double-walled immersion well.

The efficiency of this type of reactor is very high since the lamp is effectively surrounded by the reacting solution. The lamp is contained in a double-walled Quartz immersion well through which water is passed for cooling.

Two basic types of mercury lamp were used. Low pressure lamps (6 or 16W rating) emit 90% of their radiation at 254nm. High pressure lamps (125W) radiate predominantly at 365-6nm radiation.

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C NMR were recorded using a 270 MHz Joel spectrometer.The solvents used were DMSO-d^{6}(hexadeuterio -dimethylsulphoxide) , $CDCl_3$ (deuteriochloroform) and C_5D_5N (heptadeuteriopyridine).
The reference for ^{1}H NMR was trimethylsilane (TMS ; δ=0).

Elemental Analyses

C , H and N analyses were acrried out by Butterworth Laboratories Ltd. of Teddington , Middlesex.

Part 1. Syntheses involving the cyclisation of enamides.

2-Indanone (168)

2-Indanone (168) was prepared following the method of Rosen, Dorfman and Linfield[89]. 90% Formic acid (175ml), water (9ml) and 35% hydrogen peroxide (30ml) were added in this order to a 500ml flask, and were stirred and warmed to 35°C over a period of 15 minutes.

Indene (29.05g, 0.25 mol) was added over 2 hours, the reaction temperature being maintained at 35-40°C by gentle water cooling. The reaction mixture was stirred at 35°C for a further hour, and then at room temperature overnight followed by addition of a fresh solution of ferrous sulphate heptahydrate (5.3g) in water (26.5ml). The dark amber solution was concentrated to a third of original volume under reduced pressure and diluted with a warm solution of concentrated sulphuric acid (70ml) in water (430ml), and the mixture was steam distilled. When distillation was complete, the distillate turned from cloudy to clear. Approximately 1.5 litres of distillate were collected and left overnight. 2-Indanone was collected, by filtration, in the form of white needles. The filtrate was extracted with D C M (3 x 50ml) and the combined extracts were washed with water and dried over sodium sulphate (anhydrous). The combined extracts were rotor-evaporated to dryness, when 2-indanone was obtained as a white solid lump in good yield, 19.8g (60%) which had a mp 55-57°C (Lit[89] 57-58°C) T L C, Rf 0.83, $M^{+\cdot}$ 132 (Appendix 1.7). Infrared νC=O 1710 (s), νCH 2900, 3010 (w) cm^{-1}.

1-Acetamido-2(1'-indenyl)indene (184)

This was prepared using the method of Smith[77]. 1-indenone (13.2g , 100mmol) and acetamide (2.95g, 50mmol) were heated together in refluxing toluene (150ml) containing toluene-4-sulphonic acid (100mg) under a Dean and Stark trap. After 27 hours, the excess of toluene was removed and the residue cooled.

The crystalline material which separated out was collected and recrystallisation from ethanol afforded 1-acetamido-2(1'-indenyl)indene (184) (6.26g, 44%) which had mp 196-7°C (lit[77] 197-199°C). T L.C ,Rf 0.70 . $M^{+\bullet}$ 287 (appendix 1.4), Infrared ν NH 3260 (s), ν C=O 1645 (s), ν CH 3050 - 3000 cm^{-1}.

Hydrolysis of 1-acetamido-2(1'-indenyl)indene (184)

1-Acetamido-2(1'-indenyl)indene (0.6g, 3.2 mmol), dissolved in tetrahydrofuran (45ml) was treated with hydrochloric acid (6M , 45ml) and the solution was then heated at 45°C for 10 hours. Removal of the solvent gave a crude solid, which after recrystallisation from acetic acid afforded 2(1'-indanylidenyl)indan-1-one (185), (0.192g , 38%), which had m.p. 140-142°C (Lit[87] 141-143°C), T L C ,Rf 0.53 , $M^{+\bullet}$ 246 (appendix 1.7) , Infra-red νC=O 1675 (s) , νCH 2950-3040 (w) cm^{-1}.

1-Acetamido-2(1'-indenyl)indene (184)

This was prepared using the method of Smith[77]. 1-indenone (13.2g , 100mmol) and acetamide (2.95g, 50mmol) were heated together in refluxing toluene (150ml) containing toluene-4-sulphonic acid (100mg) under a Dean and Stark trap. After 27 hours, the excess of toluene was removed and the residue cooled.

The crystalline material which separated out was collected and recrystallisation from ethanol afforded 1-acetamido-2(1'-indenyl)indene (184) (6.26g, 44%) which had mp 196-7°C (lit[77] 197-199°C). T L C ,Rf 0.70 . $M^{+\bullet}$ 287 (appendix 1.4), Infrared ν NH 3260 (s), ν C=O 1645 (s), ν CH 3050 - 3000 cm^{-1}.

Hydrolysis of 1-acetamido-2(1'-indenyl)indene (184)

1-Acetamido-2(1'-indenyl)indene (0.6g, 3.2 mmol), dissolved in tetrahydrofuran (45ml) was treated with hydrochloric acid (6M , 45ml) and the solution was then heated at 45°C for 10 hours. Removal of the solvent gave a crude solid, which after recrystallisation from acetic acid afforded 2(1'-indanylidenyl)indan-1-one (189), (0.192g , 38%), which had m.p. 140-142°C (Lit[87] 141-143°C), T L C ,Rf 0.53 , $M^{+\bullet}$ 246 (appendix 1.7) , Infrared νC=O 1675 (s) , νCH 2950-3040 (w) cm^{-1}.

Attempted preparation of 1-propionamido-2(1'-indenyl)indene.

1-Indanone (5.0g , 38mmol) and propionamide (1.38g ,19mmol) were heated together in refluxing toluene (150ml)under a Dean and Stark trap for 72 hours.The precipitate which separated out on cooling, was washed with saturated sodium bicarbonate solution (2 x 50ml) and water (2 x 50ml) and rotor-evaporated to dryness. The'product' was obtained in good yield.

The M.S. did not give the expected molecular ion $M^{+\cdot}$301, but a molecular ion of $M^{+\cdot}$342 instead (appendix I.11)

Attempted preparation of 1-benzamido-2(1'-indenyl)indene.

1-Indanone (5.0g ; 38 mmol) and benzamide (2.29g ; 19 mmol) were heated together under a Dean and Stark trap, in refluxing toluene (150 ml) containing toluene-4-sulphonic acid (100mg) for 90 hours.
The reaction mixture was cooled, washed , dried and then rotor-evaporated to dryness. Evidence from mass spectrometry and infrared spectroscopy indicated that the product was benzamide, Mass spectrometry indicated that a small amount of unknown product was present, which had a M^{+} 342 (appendix I.11). Yield of unknown product was 51% with a m.p. $>260^{o}$C (Kofler). TLC Rf 0.76. Infrared $\supset$C=C 1610 cm^{-1}. Found: C, 94.68 ; H, 5.39 % . $C_{27}H_{18}$ requires C, 94.73 ; H, 5.26 %.

By comparison of mass spectra (appendix I.11) with published data , it was confirmed that the product formed by the self-condensation of 1-indanone (132) with the amides - propionamide, benzamide and cinnamamide - results

in the formation of the trimer condensation product of 1-indanone namely Truxene or 10,15-Dihydro-5H-diindeno-[1,2-a;1',2'-c] fluorene, (193)

Attempted preparation of 1-cinnamamido-2(1'-indenyl)-indene (202)

1-Indanone (1.0g, 7.5 mmol) and cinnamamide (0.557g, 3.75 mmol) were heated together under a Dean and Stark trap, in refluxing toluene (150ml) containing toluene-4-sulphonic acid (100mg) for 150 hours.
The resulting solution was washed, dried and rotor-evaporated to dryness. The resulting crystalline product was found to be cinnamimide as evidenced by IR and mass spectrometry. Also mass spectrometry showed that an unknown product was present with $M^{+\bullet}$ 342 (appendix 1.11). This compound by mass spectra comparison with compound (193) was found to be 'Truxene'.

2-Acetamido-1(2'-indenyl)indene (185)

The above method of Smith[77] was used, 2-indanone (168), (13.2g, 100mmol) being used instead of 1-indanone (132).
After 20 hours the excess of toluene was removed and the mixture was cooled in an ice-bath. Crystalline material rapidly separated out and was collected by filtration. Recrystallisation from acetic acid afforded 2-acetamido-1(2'-indenyl)indene (9.7g, 76%) which had mp 226-9°C (Lit[77] 228-30°C). T L C, Rf 0.56. $M^{+\bullet}$ 287 (appendix 1.5). Infrared ν_{NH} 3295 (s), ν_{CH} 3020-40 (w), $\nu_{C=O}$ 1665 (s) cm^{-1}.

2-Propionamido-1(2'-indanyl)indene (190)

2-Indanone (5.0g, 38 mmol) and propionamide (1.38g, 19mmol) were heated together under a Dean and Stark trap in refluxing toluene containing the catalyst-toluene-4-sulphonic acid (100mg) for 72 hours.

The mixture was cooled in an ice-bath when crystals separated out. These were collected and dried. The filtrate was rotor-evaporated, after washing with saturated sodium bicarbonate solution (2 x 50ml), to dryness and these crystals were also collected.

The crystals were recrystallised from ethyl acetate to afford 2-propionamido-1(2'-indenyl)indene (5.7g, 23%) which had mp 210-12°C. T L C, Rf 0.65, $M^{+\bullet}$ 301 (appendix 1.8), Infrared ν_{NH} 3300, Amide I, II 1610, 1660 cm^{-1}. Found C,83.63 ; H, 6.23 ; N, 4.61 %. $C_{21}H_{19}NO$ requires C,83.72 ; H, 6.31 ; N, 4.65 %.

2-Benzamido-1(2'-indenyl)indene (191)

The above experiment was repeated using the amide benzamide (2.29g, 19mmol) instead of propionamide. The mixture was refluxed with toluene-4-sulphonic acid (100mg) for 90 hours. Work-up of the reaction mixture as above afforded 2-benzamido-1(2'-indenyl)indene (3.19g, 48%) which had mp 215-6°C. T L C, Rf 0.78, $M^{+\bullet}$ 349 (appendix 1.9). Infrared ν_{NH} 3300, $\nu_{C=O}$ 1640 cm^{-1}. Found C,85.42 ; H,5.57 ; N,3.89%. $C_{25}H_{19}NO$ requires C,85.93 ; H,5.48 ; N,4.01%

Attempted preparation of 2-cinnamamido-1(2'-indenyl)indene

2-Indanone (1.0g,7.5mmol) and cinnamamide (0.557g ,3.75 mmol) were treated as above for 150 hours.After washing with saturated sodium bicarbonate solution (2 x 50ml) ,drying and rotor-evaporation, the resulting crystals were found to be cinnamamide , as evidenced by M.S. and I.R. A small amount of unknown product was also found, with a mass spectrum of $M^{+\cdot}$ 356 (appendix 1.12).

Hydrolysis of 2-acetamido-1(2'-indenyl)indene (185)

This method was taken from Smith[77]. 2-acetamido-1(2'-indenyl)indene (0.9g ,3.13 mmol), dissolved in tetrahydrofuran (45ml) was treated with hydrochloric acid (6M , 45 ml) and the solution was then heated at 45°C for 12 hours. Removal of the solvent afforded the crude solid, which after recrystallisation from toluene, provided the solid material - 1(2'-indanylidenyl)indan-2-one (188),(0.51g , 65%) which had m.p. 176-177°C (lit[88] 178°C), T L C , Rf 0.91 , $M^{+\cdot}$ 246 (appendix 1.6) , Infrared ν C=O 1715 , 1625 (s) , ν CH 3050 - 2900 cm^{-1}.

Hydrolysis of 2-propionamido-1(2'-indenyl)indene (190)

2-Propionamido-1(2'-indenyl)indene (1.0g , 3.32 mmol) dissolved in tetrahydrofuran (50 ml) was treated with hydrochloric acid (6M , 50ml) and the solution was heated at 45°C for 12 hours.Removal of the solvent gave a crude solid which after recrystallisation from toluene gave the solid material 1(2'-indanylidenyl)indan-2-one(188) (0.43g , 53%) , which had mp 176-177°C (Lit[88] 178°C), T L C , Rf 0.91 , $M^{+\cdot}$ 246 (appendix 1.6), Infrared ν C=O 1720 , 1640 , νCH 3035 - 2900 cm^{-1}.

Hydrolysis of 2-benzamido-1(2'-indenyl)indene (191)

2-Benzamido-1(2'-indenyl)indene (1.0g , 2.86 mmol), dissolved in tetrahydrofuran (50ml) was treated with hydrochloric acid (6M , 50ml) and the solution was then heated to 45°C for 13 hours.

Removal of the solvent gave a crude solid which was recrystallised from toluene to afford 1(2'indanylidenyl)indan-2-one (188),(0.345g ,49%), which had m.p. 177°C(Lit[88] 178°C), T L C ,Rf 0.92 , $M^{+\cdot}$ 246 (appendix 1.6), Infrared ν C=O 1720 , 1635 , νCH 3030 - 2925 cm^{-1}.

Conversion of 1(2'-indanylidenyl)indan-2-one (188)to 2-acetamido-1(2'-indenyl)indene (185)

1(2'-Indanylidenyl)indan-2-one (2.0g , 8.13 mmol) was heated with acetamide (0.5g, 8.19 mmol) in refluxing toluene in the presence of the catalyst toluene-4-sulphonic acid.Removal of the solvent followed by recrystallisation from acetic acid provided the solid 2-acetamido-1(2'-indenyl)indene (0.908g ,39%), T L C , Rf 0.56 , m.p. 227-229°C (Lit[77] 228-230°C), $M^{+\cdot}$ 287 (appendix 1.5), Infrared , ν NH 3300 , νCH 3025-3040 (w) , νC=O 1660 cm^{-1}.

Conversion of 1(2'-indanylidenyl)indan-2-one (188) to 2-propionamido-1(2'-indenyl)indene (190)

1(2'-Indanylidenyl)indan-2-one (2.0g , 8.13 mmol) and propionamide (0.59g , 8 mmol) were heated together in refluxing toluene in the presence of the catalyst toluene-4-sulphonic acid. Removal of the solvent after washing and drying provided crystalline product which was recrystallised from ethyl acetate to give 2-propionamido-1(2'-indenyl)indene (1.01g 41%) which had m.p. 211-213°C , T I C ,Rf 0.65 , $M^{+\cdot}$ 301 (appendix 1·8), Infrared νC=O 1660 , νCH 2950 , 3040 , ν NH 3300 cm^{-1}.

Conversion of 1(2'-indanylidenyl)indan-2-one (188) to 2-benzamido-1(2'-indenyl)indene (191)

1(2'-Indanylidenyl)indan-2-one (2.0g , 8.13 mmol) was heated with benzamide (0.98g , 8 mmol) in refluxing toluene containing the catalyst, toluene-4-sulphonic acid. After washing the solvent was removed by rotor-evaporation and the crystals were dried.Recrystallisation provided 2-benzamido-1(2'-indenyl)indene (0.91g,32%) which had m.p. 215-216°C, T L C , Rf 0.78 , $M^{+\cdot}$ 349 (appendix 1·9), Infrared νN-H 3300 , ν C=O 1640 cm^{-1}.

1-Acetamidoindene (182)

The method of Smith[77] was used. 1-indanone (5.0g , 38 mmol) and acetamide (2.23g , 38mmol) were heated together under a Dean and Stark trap in refluxing toluene (120ml) for 100 hours. Removal of the solvent gave a crude product of 1.02g which was recrystallised from toluene. After recrystallisation the product was still impure as evidenced by T L C and M S The impure product was obtained in 14% yield (0.76g), which had a mp of 81°C. $M^{+\bullet}$ 173 (appendix 1.2), Infrared ν NH 3195 , 3330 (s), νCH 2820 , 2940 (w), Amide I , II 1665 , 1545 cm^{-1}.

Attempted preparation of 1-propionamidoindene

The attempted preparation was carried out using the method of Ben-Ishai and Zehavi[79]. 1-indanone (5.0g , 38 mmol) and propionamide (2.77g , 38 mmol) were heated under a Dean and Stark trap in refluxing toluene (120 ml) for 130 hours. Removal of the solvent gave propionamide as evidenced by T L C , IR , MS and m.p.

Attempted preparation of 1-benzamidoindene

The method used is similar to that above. 1-indanone (5.0g , 38 mmol) and benzamide (4.58g , 38 mmol) were heated together under a Dean and Stark trap in refluxing toluene (120 ml) for 150 hours. Removal of the solvent gave benzamide as evidenced by mass spectrometry and infrared spectroscopy.

Attempted preparation of 1-cinnamimidoindene

1-Indanone (1.0g , 7.5 mmol) and cinnamimide (1.114g , 7.5mmol) were heated together under a Dean and Stark trap containing refluxing toluene (120 ml), for 150 hours. Removal of the solvent afforded cinnamimide as evidenced by mass spectrometry and infrared spectroscopy.

2-Acetamidoindene (183)

The enamide was prepared using the method of Smith[77]. 2-indanone (5.0g ,38mmol) and acetamide (2.23g , 38mmol) were heated under a Dean and Stark trap in refluxing toluene for 108 hours. Removal of the solvent gave a crude product which was recrystallised from toluene twice to give 2-acetamidoindene (3.03g, 46%) which had mp 192°C (Lit[77] 193-4°C). T L C ,Rf 0.30. $M^{+\bullet}$ 173 (appendix 1.3). Infrared νNH 3200 , 3310 , νCH 2900 , 2920 , Amide I, II 1665 , 1545 cm^{-1}

2-Propionamidoindene (192)

The enamide was prepared using the method of Ben-Ishai and Zehavi[79]. 2-indanone (5.0g, 38 mmol) and propionamide (2.77g, 38 mmol) were heated under a Dean and Stark trap in refluxing toluene (120ml) until reaction was complete as evidenced by T L C The mixture was cooled in an ice-bath where crystals rapidly separated out. The crude product was recrystallised from ethyl-acetate to afford 2-propionamidoindene (2.41g ,34%) with a m.p. 206-7°C. T L C Rf 0.53 , $M^{+\bullet}$ 187 (appendix 1.10), Infrared νNH 3190 , 3220 , νCH 2960 , 2995 , Amide I , II 1545 , 1620 cm^{-1}. Found C, 76.63 ; H, 6.84 ; N, 7.68 %. $C_{12}H_{13}NO$ requires C, 77.00 ; H, 6.95 ; N, 7.48 % .

Attempted preparation of 2-benzamidoindene

The method is similar to that above.2-indanone (5.0g, 38 mmol) and benzamide (4.58g, 38mmol) were heated together under a Dean and Stark trap, containing refluxing toluene (120 ml) for 150 hours.
Removal of the solvent gave benzamide as evidenced by mass spectrometry and infrared spectroscopy.

Attempted preparation of 2-cinnamamidoindene.

2-Indanone (1.0g , 7.5mmol) and cinnamamide (1.114g , 7.5mmol) were heated together under a Dean and Stark trap containing refluxing toluene (120 ml) for 150 hours. The resulting solution was rotoreveporated to dryness and the crystals were examined.
Evidence from both mass spectrometry and infrared spectroscopy indicate that cinnamamide was recovered(90%).

2(1'-Indanylindene)indan-1-one(189)

The ketone was prepared using the method of Bell and Spanswick[87].To a solution of sodium (0.35g) in ethanol (20ml) was added 1-indanone(2.0g , 15 mmol).The mixture was warmed on a steam bath for 20 minutes.The product was cooled, acidified and diluted with acetic acid.The sticky precipitate was first recrystallised from ethanol and then twice from acetic acid to yield 2(1'-indanylidene)indan-1-one (2.39g , 64%) which had mp 141-2°C (Lit[87] 141-2°C). T L C ,Rf 0.56 ,$M^{+\cdot}$246 (appendix 1.7). Infrared $\nu_{C=O}$ 1680 (s), ν_{CH} 2940 , 3050 (w) cm^{-1}.

1(2'-Indanylidene)indan-2-one (188)

The ketone was prepared using the method of Treibs and Schroth[88].To a 10% solution of sodium methoxide in dry methanol was added 2-indanone (1.0g , 7.5mmol).The mixture was stirred and heated under reflux for 2 hours.The basic solution was neutralised with acetic acid (4ml).The crystals which formed were collected by filtration and washed with water and dried over sodium sulphate.The green crystals of (188) were obtained in good yield (1.39g,75%) which had mp 177-8°C (Lit [88] 178°C).T L C ,Rf 0.91 , $M^{+\bullet}$ 246 (appendix 1.6),Infrared νC=O 1725, 1635 (s) , ν CH 3070 , 2950 (w) cm^{-1}.

Attempted self-condensation of 2-indanone (168)

2-Indanone (5.0g,38mmol) was heated in refluxing toluene (180ml) containing toluene-4-sulphonic acid (200mg) for 48 hours under a Dean and Stark trap.On cooling a precipitate separated out which was collected,dried and after recrystallisation from dimethyl formamide yielded a product with $M^{+\bullet}$360, (2.37g , 52%) which had a mp 215°C with decomposition (Kofler).T L C ,Rf 0.76 . Infrared νC=C 1630, 1698 cm^{-1}.Found C,91.06 ;H,5.21 %.$C_{27}H_{18}O$ requires C,90.0; H,5.0 %. $M^{+\bullet}$360 (appendix 1.13).

Rotor-evaporation of the filtrate gave a solid(2.5g) which, by mass spectal and mp comparison, was found to be starting material, 2-indanone.

2-Acetamido-1(2'-indenyl)indene(185)

2-Acetamidoindene (0.7g , 4mmol) was reacted with 2-indanone (1.0g ,7.5mmol) in the presence of toluene-4-sulphonic acid in refluxing toluene for 90 hours. Removal of the solvent and recrystallisation from acetic acid provided 2-acetamido-1(2'-indenyl)indene (185), (1.158g ,76%) , which had m.p. 228-229°C (Lit[77] 228 - 230°C), $M^{+\cdot}$ 287 (appendix 1.5) , Infrared ν NH 3295 (s) , ν CH 3020-3040 (w) , ν C=O 1660 (s) cm^{-1}.

2-Propionamido-1(2'-indenyl)indene (190)

2-Propionamidoindene (1.0g , 5.34 mmol) was reacted with 2-indanone (0.70g, 5.3 mmol) in the presence of of toluene-4-sulphonic acid , in refluxing toluene, for 70 hours. Removal of the solvent after washing and drying afforded the crude solid, which on recrystallisation from ethyl acetate provided 2-propionamido-1(2'-indenyl)indene (1.09g ,68%),which had m.p. 211-212°C , T L C , Rf 0.65 , $M^{+\cdot}$ 301 (appendix 1.8), Infrared νN-H 3300 (s) , Amide I , II 1660 , 1610 cm^{-1}.

Time Study of the prepataion of 2-Propionamido-1(2'-indenyl)indene (190)

Propionamide (1.38g ; 19mmol) and 2-indanone (5.0g ; 38 mmol) were heated together in refluxing toluene in the presence of p-tosic acid. Samples were taken every ½ hour.

By comparison with authentic 2-propionamidoindene, TLC examination confirmed that the preparation of 2-propionamido-1(2'-indenyl)indene (190) proceeded via route 1, as

2-propionamidoindene was formed during the reaction, and not the corresponding dimer ketone (188).

Taking the reaction to completion (72hours) resulted in the formation of 2-propionamido-1(2'-indenyl)indene (58%), which had m.p. 211-212°C, TLC Rf 0.65 , $M^{+\cdot}$ 301 (appendix 1.8) , Infrared ν N-H 3300 (s) , Amide I , II 1660 , 1610 cm^{-1}.

Conversion of 2(1'-indanylidenyl)indan-1-one (189)to 1-acetamido-2(1'-indenyl)indene (184)

2(1'-Indanylidenyl)indan-1-one (2.0g, 8.3 mmol) was heated with acetamide (0.5g, 8.19mmol) in refluxing toluene, in the presence of the catalyst, toluene-4-sulphonic acid for 48 hours.

Removal of the solvent gave the crude product,which after recrystallisation from ethanol, afforded 1-acetamido-2(1'-indenyl)indene (1g , 43%) which had m.p. 198°C (Lit[7] 197-199°C), T L C ,Rf 0.70 , $M^{+\cdot}$ 287 (appendix 1.4), Infrared ν C=O 1640 (s) , ν CH 3050-3010 (w) , ν NH 3260 cm^{-1}

Self-condensation of 1-indanone (132)

1-Indanone (5.0g , 38mmol) was heated in refluxing toluene (180ml) containing toluene-4-sulphonic acid (200mg) for 96 hours under a Dean and Stark trap.On cooling a small amount of yellow precipitate was collected,Mass spectra and elemental analysis evidence suggests that this is (193) or Truxene (1%) which had mp 260°C (kofler). T L C ,Rf 0.76 . $M^{+\cdot}$ 342 (appendix 1.11). Infrared ν C=C 1608 cm^{-1}. Found : C, 94.68 ;H, 5.39 %.$C_{27}H_{18}$ requires C,94.73 ; H, 5.26%.

The remaining filtrate was washed , dried and rotor-evaporated to dryness. The resulting solid (3.75g,83%) had

m.p. 132°C (Kofler) , T L C ,Rf 0.66, $M^{+\bullet}$ 356 (appendix I·II) Infrared νC=O 1612 , 1679 cm^{-1}.Found: C, 87.21 ; H, 5.61%. $C_{27}H_{16}O$ requires C, 91 ; H, 4.49 %.

Self-condensation of 1-indanone (132).

1-indanone (1.0g ; 7.5 mmol) was heated with p-tosic acid in refluxing toluene. After 4 days the reaction was stopped. Removal of the excess of solvent gave a small amount of solid which was identified as Truxene, by m.p. and TLC comparison with authentic material, in poor yield (1%).m.p. > 340°C ,. TLC Rf 0.53.

Self-condensation of 1-indanone for a short period of time.

The reaction conditions are exactly as above, except the reaction was stopped after 48 hours.
On cooling a yellow precipitate was obtained , which was collected and dried.

The remaining solution was washed with water and dried. Rotor-evaporation to dryness afforded a yellow solid.

Recrystallisation from acetic acid afforded, in each case , 2(1'-indanylidenyl)indan-1-one (189) (95%), which had m.p. 141-143°C(Lit[87] 141-142°C), T L C , Rf 0.35 ,$M^{+\bullet}$ 246 (appendix I·7) , Infrared νC=O 1675 , νCH 2940 , 3051 cm^{-1}.

Self-condensation of 1-indanone for a long period of time.

1-Indanone (1.0g , 7.5mmol) was refluxed in toluene (120 ml) containing toluene-4-sulphonic acid (80mg) for 168 hours. After this time the reaction was stopped. On cooling, a yellow precipitate separated out, which was collected and dried. Analysis indicated that 'Truxene' was obtained (65%), which had m.p. > 340°C, T L C , Rf 0.53 , $M^{+\cdot}$ 342 (appendix I·II), Infrared δCH_2 1387 , 1467 ; δCH 732 cm^{-1}.

The remaining solution was washed with water(3 x 30ml) and dried. Rotor-evaporation to dryness afforded 2(1'-indanylidenyl)indan-1-one (189),(25%), which had m.p. 141-143°C(Lit[87] 141-142°C) , T L C , Rf 0.55, $M^{+\cdot}$ 246 (appendix I·7), Infrared $\delta C=O$ 1672 , δCH 2939 , 3050 cm^{-1}.

Conversion of 2(1'-indanylidenyl)indan-1-one to 'Truxene' (193)

2(1'-Indanylidenyl)indan-1-one (100mg) was refluxed in toluene containing toluene-4-sulphonic acid (15mg) for 120 hours, after which time, the reaction was stopped. On cooling, a precipitate separated out, which was collected and dried. Mass spectra indicates that the compound is 'Truxene' (193),(56%), which had m.p. > 340°C, T L C , Rf 0.53, $M^{+\cdot}$ 342 (appendix I·II), Infrared δCH_2 1390 , 1470 ; δCH 735 cm^{-1}.

The remaining solution was washed with water and dried. Rotor-evaporation to dryness and recrystallisation from acetic acid afforded 2(1'-indanylidenyl)indan-1-one (189), (13%), which had m.p. 142-143°C(Lit[87] 141-142°C), T L C , Rf 0.35 , $M^{+\cdot}$ 246 (appendix I·7), Infrared $\delta C=O$ 1672 , δCH 2940 , 3050 cm^{-1}.

Attempted preparation of 2-acetamidoindene.

Freshly prepared 2-indanone (5.0g ; 38 mmol) and acetamide (2.23g ; 38 mmol) were heated together under a dean and stark trap in refluxing toluene for 96 hours. Removal of the solvent afforded 2-indanone, recovered in 82% yield, which had m.p. 56-57°C (Lit[89] 57-58°C), TLC Rf 0.83 , $M^{+\cdot}$ 132 (appendix 1.1), Infrared ϑC=O 1710 (s) , ϑCH 2900 , 3010 (w) cm^{-1}.

Preparation of 2-acetamidoindene,

2-Indanone (supplied by Aldrich, purity 75%), (5.0g ; 38 mmol) and acetamide (2.23g ; 38 mmol) were heated together in refluxing toluene for 96 hours.
Removal of the solvent afforded 2-acetamidoindene in poor yield (7%), which had m.p. 192-193°C (Lit[77] 193-194°C), TLC Rf 0.30 , $M^{+\cdot}$ 173 (appendix 1.3) , Infrared ϑNH 3200 , 3310, ϑCH 2900 , 2920 , Amide I , II 1665 , 1545 cm^{-1}.

Attempted preparation of 2-acetamidoindene.

2-Indanone was freshly prepared and allowed to 'age' by leaving the ketone in air. The attempted condensation between 2-indanone (5.0g ; 38mmol) and acetamide (2.23g ; 38 mmol) was carried out in refluxing toluene for 96 hours. Removal of the excess solvent afforded only the starting ketone, in yields between 80 - 90 % .
The above experiment was carried out every five days, for example using 5 day old , 10 day old , 15 day old etc. 2-indanone. Tha last experiment was carried put using 99 day old 2-indanone.On no occasion was 2-acetamido-indene formed, instead, only the ketone was recovered.

Part 2. Syntheses involving the Wolff rearrangement of benz[h]quinolin-5,6-diazoketone.

Benz[h]quinolin-5,6-dione (99)

Benz[h]quinolindione was prepared according to the method of Kloc et al [17]

Benz[h]quinoline (13.4g , 75 mmol) was dissolved in acetic acid (300 ml) to which iodine pentoxide (26.2g) was added with stirring. The solution, pale orange in colour, was refluxed with stirring for 2 hours. The excess iodine pentoxide was removed by filtration, and iodine as well as acetic acid were removed from the filtrate by rotorevaporation to dryness.

The orange solid which remained was collected and dried. 3.0g of impure dione were transferred to an extraction thimble and soxhlet extracted into chloroform (280 ml). After extraction was complete, the extract was washed with 10% w/v sodium thiosulphate (100ml), distilled water (100ml) and then back extracted with chloroform (50ml). The final extract was dried over sodium sulphate and then rotor-evaporated to dryness.

Recrystallisation from ethanol afforded pure benz(h)-quinolindione. The remaining dione (11.8g) was purified following the above procedure.

Benz[h]quinolin-5,6-dione (40%) had m.p. 214°C (Lit[17] 214-215°C), T L C , Rf 0.5 (1b), $M^{+\bullet}$ 209 (appendix 1.14) , Imfrared ν C=O 1690 , 1675 cm^{-1}.

Kloc[17] et al proposed an alternative method of purification of the impure dione.

After rotor-evaporation of acetic acid, benzene (100ml) was added to the residue and then distilled off together with any remaining iodine.This was repeated until the distillate was colourless.

The crude product was decolourized by heating with carbon and after drying was recrystallised from ethanol to give the orange needles of benz[h]quinolin-5,6-dione, 35% (m.p., IR , MS and TLC as before).

As the yields of purification were so low, attempts were made to purify the dione by flash chromatography.

Dione (0.5g) was dissolved in dimethyl formamide(2ml), and placed on top of the column.The column(20 x 250mm) was dry packed with stationary phase,(Kiselgel 60 , 230 - 400 mesh), 60g; with eluent ethyl acetate(25%), petroleum ether (40 - 60)(75%). The flow rate was maintained at 10.5 ml min^{-1} and the % of ethyl acetate was gradually increased until the final eluent was 100% ethyl acetate.

The fractions were collected and examined by T L C (1b) and those containing solutes with similar Rf values were combined.The dione obtained by this purification gave a different Rf value as well as a different melting point. The initial m.p. was 207°C which was raised to 209°C by recrystallisation from ethanol (Lit[17] 214 - 215°C), T L C , Rf 0.94 (1a) (Ref pure dione 0.82), 32% yield (160mg recovered).

Benz[h]quinolin-5,6-dionium chloride (206)

The dione (3.0g ; 14.4 mmol) was disoolved in refluxing chloroform (80ml) and this solution was heated with decolourising charcoal (1.0g), then cooled and filtered. The chloroform solution which resulted was stirred in an ice-bath and hydrogen chloride gas was bubbled into it ata steady rate for 20 minutes.The crude product was washed with diethyl ether and then dried in vacuo.
The infrared spectrum of the crude salt demonstrated a marked shift in the carbonyl stretching frequencies (ν max C=O 1730 , 1700 cm^{-1}.)
Recrystallisation from methylcyanide gave the free bases, which had a m.p. of 214°C.Pure benz[h]quinolin-5,6-dione was obtained in 62% yield.T L C , Rf 0.5 (1b), Infrared νC=O 1690 , 1675 cm^{-1}.

Benz[h]quinolin-5,6-diazoketone(186)

Benz[h]quinolin-5,6-dione (503mg ; 2.4mmol) was suspended in a solution of toluene-4-sulphonylhydrazide (482mg) in ethanol(10ml) and was then heated for 65 minutes at 40 - 50°C.
The resulting solution was cooled in an ice-bath and the white precipitate was collected by filtration.
Recrystallisation from methanol afforded pure benz[h]-quinolin-5,6-diazoketone (75%), which had m.p. 142-3°C, (Lit[7] 142-5°C),T L C ,Rf 0.61 (1a), $M^{+\cdot}$ 221 (appendix 1.15), Infrared νN=N 2110 , νC=O 1640 cm^{-1}.

Part i. Wolff rearrangement of benz[h]quinolin-5,6-diazoketone induced by Thermolysis.

Rearrangement A.

Benz[h]quinolin-5,6-diazoketone (1.0g ,4.5mmol) was dissolved in a mixture of benzyl alcohol(5ml) and dimethylaniline (5ml).The solution was rapidly heated by immersing the reaction flask into a pre-heated oil bath at 180°C. After a few seconds nitrogen gas began to evolve.Heating was continued up to 190°C for 5 minutes when the evolution of nitrogen ceased.
The solution was cooled and ether (15ml) was added.
The extract was washed with dilute hydrochloric acid (2 x 10ml) and distilled water (3 x 10ml).
The acid extract was basified and extracted into ether (2 x 10ml).The etheral extracts were combined and after drying their volume was reduced by rotor-evaporation to 3 ml.
Several products were present as evidenced by T L C , (1a).Attempts were made to separate them by flash chromatography.
The column (20 x 250 mm) was dry packed with the stationary phase, 60 g (Kiselgel 60; 230-400 mesh) and the initial eluent was 5%ethyl acetate/95% petroleum ether.
The flow rate was maintained at 11.3 ml min^{-1}, and the ratio of ethyl acetate,after several fractions had been collected was raised to 10%.
The final fractions were collected using acetic acid as eluent.

The fractions were collected and examined by T L C (1a), and those containing solutes with similar Rf values were combined.

Fraction I

Rf 0.63

IR No νC=O stretching frequencies

MS No indenopyridine fragments present

Fraction II

Rf 0.33

IR ν C=O 1740 cm^{-1}

MS No indenopyridine fragments present

Fraction III

Rf 0.23

IR ν C=O 1740 cm^{-1}

MS Indenopyridine fragment observed at m/z 181 (Appendix 1.16)

Fraction IV

Rf 0.05

IR νC=O 1715 cm^{-1}

MS m/z=301 was present along with other fragments, but appeared impure (appendix 1.17).

The small amount of product which appeared to be present, however, could not be purified further.

Rearrangement B.

Diazoketone(0.5g ,2.26mmol), was dissolved in a mixture of ethanol(7.5ml) and triethylamine (7.5ml) and was refluxed. The resulting solution was examined by T L C (1c) and I.R. at regular intervals.
After 8 hours the reaction was stopped.From T L C , the main component was found to be the starting diazoketone (Rf 0.16), a very small amount of possible product was also evidenced at Rf 0.24, but from IR spectroscopy, no carbonyl ester groups were present.

Further refluxing did not alter this situation.Removal of the solvent gave the diazoketone (87%).

Rearrangement C.

The diazoketone (200mg,0.9mmol),was dissolved , with stirring, into ethanol (10ml) and the resulting solution was refluxed for 9 hours.After this time no reaction had occurred, as evidenced by T L C (1c) and infra-red.
Removal of the solvent gave the diazoketone(m.p. 145°C (Lit[77] 142-5°C) in 93% yield.

Rearrangement D.

The diazoketone (0.5g ; 2.26mmol) was dissolved in benzyl alcohol (15ml) and the resulting solution was refluxed for 12 hours,after which time the major product was the diazoketone (Rf 0.63 , 1a).
The solution was split.One half was placed in an ultrsonic bath for 30 minutes, after which time there was no change.

The other half was acidified with 2M HCl, after which the solution turned from dark red to yellow in colour. The solution was extracted into ether (2 x 10ml), basified with 2M NaOH and then extracted into chloroform (25ml).The resulting chloroform extract, blue in colour, was rotor-evaporated to a final volume of 3ml .

Several products were evidenced by T L C (1a), these were separated by preparative T L C , using 1a as the mobile phase.

The four products which were observed were scraped from the plates and placed into centrifuge tubes.

They were extracted with chloroform (15ml) by centrifuging for 15 minutes at 1.5 x 1000 ↻/min(R.P.M.)

Each of the four extracts were examined by IR spectroscopy. None of the fractions were found to contain a carbonyl ester absorption.

Mass spectrumof each of the fractions also confirmed this, also that no indenopyridine fragments were present.

This led me to believe that the desired ester was not present in any of the four fractions.

Part ii. Wolff rearrangement induced by Photolysis

9-Diazo-10-phenanthrone (195)

The diazoketone was prepared according to the method of Cava et al[102]. 9,10-phenanthraquinone (1.4g ; 6.7mmol) was suspended in a solution of toluene-4-sulphonylhydrazide (1.246g ; 6.7mmol) in ethanol(15ml).

The solution was refluxed until all the dione had dissolved . The solution was allowed to cool and yellow crystals precipitated out.Recrystallisation from methanol afforded pure 9-diazo-10-phenanthrone (53%),which had m.p. 107°C(Lit[102] 107-109°C),T L C ,Rf 0.66 (1a), Infrared $\nu_{N=N}$ 2100 ,$\nu_{C=O}$ 1628 cm^{-1}, $M^{+\cdot}$ 220 (appendix 1·18).

9H-Fluorene-9-tertbutylcarboxamide (197)

The amide was produced according to the method of Kinson and Trost[101].

9-diaza-10-phenanthrone (0.67g ; 3.04mmol) and tertbutylamine (0.222g , 3.04mmol) were dissolved in toluene (150ml) contained in a photolysis reaction flask. The solution was deoxygenated for 40 minutes using a nitrogen purge.The apparatus was warmed in a water bath at 40°C and irradiated for 20 hours using a l.p. mercury lamp (6W).

After this period the solution was cooled and removal of the solvent afforded fawn crystals(m.p. 154°C) Recrystallisation from ethanol afforded pure 9H-fluorene-9-tertbutylcarboxamide (86%) which had m.p. 158°C,T L C , Rf 0.6 (1a), Infrared ν_{N-H} 3265 , amide I and II 1650 , 1555 cm^{-1}, $M^{+\cdot}$ 265 (appendix 1·19)

Attempted preparation of 5H-indeno[1,2-b]pyridine-5-N-tertbutylcarboxamide (211)

Benz[h]quinolin-5,6-diazoketone (450mg ; 2.03 mmol) and tertbutylamine (148mg ; 2.03 mmol) were dissolved in toluene (150 ml) contained in a photolysis reaction flask. The solution was deoxygenated for 50 minutes with a nitrogen purge,The apparatus was irradiated for 25 hours using a low pressure mercury lamp (6W).

Examination of the reaction mixture by T L C showed that apart from the starting diazoketone, only one other product was visible with a Rf of 0.62, this however appeared to be in small yield.

The experiment was continued for a further 24 hours, the reaction being followed by T L C with samples being taken every 5 hours.

The last of these samples, taken after 24 hours, was seen to contain four components. Two of these components came from the diazoketone itself (Rf 0.37 , 0.51), the other two being products, Rf 0.67 ; 0.14.

The reaction was stopped after a total time of 49 hours and the solution was transferred to a RBF. Crystals were seen to appear on the photolysis tube as the solvent evaporated off.These were collected and dried in a desiccator.

The solution in the flask was reduced in volume and the components were separated by preparative T L C using petroleum spirit (40-60) 66% and ethyl acetate 34% , as the mobile phase.

Each product band was scraped from the plates and placed into centrifuge tubes. They were extracted with chloroform (15ml) by centrifuging for 10 minutes at 1.5 x 1000 ↻/min. (R.P.M.).

As evidenced by infrared spectroscopy, none of the fractions contained ↻C=O amide absorptions and mass spectrometry of each of the fractions also confirmed that the desired product was not obtained as no fragments indicative of an indenopyridine were present.

Attempted preparation of (211)

Benz[h]quinolin-5,6-diazoketone (450mg ; 2.03mmol) and tertbutylamine (148 mg; 2.03mmol) were dissolved in toluene (100ml) contained in a photolysis reaction flask. The solution was deoxygenated for 30 minutes using a nitrogen purge. The apparatus was warmed to 40°C in a water bath and irradiated for 72 hours using a low pressure lamp (6W).

A leak in the apparatus led to the introduction of water in to the reaction mixture, hence two layers were obtained. Both the aqueous layer and the toluene layer were collected and reduced in volume, and examined by T L C.

The aqueous fraction contained one component which had a Rf of 0.08. Mass spectrometry and infrared data showed that the expected component (211) was not present.

The toluene fraction contained two major components accompanied by many minor products. Purification by preparative T L C gave three components with Rf values of 0.62 ; 0.46 ; 0.36.

Mass spectra examination showed that two of the components (Rf 0.46 , 0.36) contained fragments indicative of an indenopyridine (m/z 181 , 153 ; appendix I.20).

The desired product, however , was not present.

Attempted preparation of methyl(RS)-5H-indeno[1,2-b]-pyridine-5-carboxylate (187).

This reaction was carried out according to the method of Smith[77]. Benz[h]quinolin-5,6-diazoketone (300mg ; 1.4mmol) was dissolved in tetrahydrofuran (120ml) and methanol(70ml) contained in a photolysis reaction flask. The solution was deoxygenated for 30 minutes using a nitrogen purge.
The apparatus was irradiated for 4 hours using a low pressure mercury lamp (6W).The volume of the reacting solution was too great to enable suitable photolysis to occur (only 50% was being subjected to UV radiation) so the mixture was split.
Irradiation of the first half (experiment a) was continued with a low pressure lamp for 30 hours whilst, irradiation of the second half (experiment b) was continued for a further 24 hours using a high pressure mercury lamp(125W).
Both reaction mixtures (a and b) were examined by T L C
Reaction mixture a was found to contain 3 components with Rf values 0.66 ; 0.55 ; 0.42.
Reaction mixture b, also contained 3 components with Rf values 0.66 ; 0.42 ; 0.26 .
Both solutions were reduced in volume and the components were separated by preparative T L C. The resulting solutes of similar Rf were combined and examined by mass spectrometry.
The solute with Rf 0.66 contained fragments at m/z 181 , 153 indicative of an indenopyridine .

The solute with Rf 0.55 contained fragments at m/z 182 , 154 , indicative of an indenopyridine structure , and also m/z 241 (appendix I.21)

The solute with Rf 0.42 had a fragment at m/z 448 , (appendix I.22).

The mass of the desired product was 241, but a dimer might possibly occur at 448.

Further purification of these solutes by flash chromatography proved unsuccessful.

The previous experiment was repeated at temperatures of $0^{o}C$ and $40^{o}C$, the apparatus being irradiated with a high pressure lamp for 72 hours.

At $0^{o}C$, removal of the solvent afforded three components, as observed by TLC, which had Rf values 0.55 ; 0.42 and 0.26. The components were separated by preparative TLC and extracted with Chloroform.These extracts were then examined by mass spectrometry.

All three components were found to contain fragments indicative of an indenopyridine , as well as a fragment at m/z 225 (appendix I.21 ; I.22 and I.23).

The fraction with Rf 0.42 , was also found to conatin a fragment with m/z 448, which might indicate the presence of the dimer (194).

Further attempts to purify the fractions by flash chromatography were unsuccessful.

The previous experiment was repeated at 40°C by warming the apparatus to 40°C in a water bath.
Removal of the solvent , followed by examination by TLC gave three components with Rf values 0.77 ; 0.57 and 0.18. The components were separated by preparative TLC and extracted with chloroform.
These extracts were then examined by mass spectrometry. The components with Rf 0.77 and 0.57 were found to contain fragments indicative of an indenopyridine as well as a fragment at m/z 225 (appendix I.24 and I. 25). The latter extract (Rf 0.18) did not contain any such fragment.

Further purification by flash chromatography was unsuccessful.

Attempted preparation of (211).

Benz[h]quinolin-5,6-diazoketone (300 mg ; 2.03 mmol) and tertbutylamine (100 mg ; 2.03 mmol) were dissolved in toluene (120ml) in a photolysis reaction flask, which was purged with nitrogen for thirty minutes .
The apparatus was irradiated at room temperature for four hours using a high pressure lamp.

After this time the solution was examined by T L C (1a), two components were observed : starting material (Rf 0.63) and possible product at Rf 0.39.
Infra-red, however, showed that this product had no carbonyl amide absorption and mass spectral examination did not give any indenopyridine fragments nor the desired product ion of 267.

Attempts to purify the product by flash chromatography proved fruitless.

Attempted photolysis of benz[h]quinolin-5,6-dione(99)

Benz[h]quinolin-5,6-dione (400mg ; 1.9mmol) was dissolved in methanol (70ml) and tetrahydrofuran (120ml) contained in a photolysis reaction flask.The solution was deoxygenated using a nitrogen purge.
The apparatus was warmed to 40°C in a water bath and irradiated for 196 hours using a high pressure mercury lamp (125W).
After this period the reaction was cooled and the solvent removed to yield the dione (m.p. 214°C,Lit[17] 214-215°C).

The experiment was repeated as above except that the dione (400mg ; 1.9mmol) was dissolved in toluene (140ml) and the resulting solution was irradiated at 40°C for 120 hours with a high pressure lamp.
After this period the reaction mixture was cooled,removal of the solvent gave unchanged dione (m.p. 214°C,Lit[17] 214-215°C.)

Attempted photolysis of benz[h]quinolin-5,6-diazoketone

Benz[h]quinolin-5,6-diazoketone (400mg ; 1.8mmol) was dissolved in toluene (140ml) contained in the photolysis reaction flask.The solution was deoxygenated using a nitrogen purge.

The apparatus was irradiated at room temperature for 144 hours using a low pressure mercury lamp (6 W).

After this period the solvent was removed to give 73% recovery of the diazoketone (m.p. 143-144°C. Lit[77] 143-144°C).

The above experiment was repeated with the diazoketone (300mg ; 1.4mmol) dissolved in tetrahydrofuran (120ml) and methanol(70ml).

The apparatus was warmed to 40°C and irradiated for 196 hours using a low pressure lamp (6W).

After this period of time, the reaction solution was cooled, removal of the solvent gave unchanged diazoketone of which 75% was recovered.The diazoketone had a m.p. of 142°C (Lit[77] 142-145°C).

Part 3. Indenopyridines from 3-methyl-2-phenylpyridine, (79).

2-Phenyl-3-pyridine carboxylic acid (158)

The preparation of (158) follows the method of DuPriest et al[24].

A mixture of 3-methyl-2-phenylpyridine (50.0g ; 0.295 mol) and potassium permanganate (140.5g ; 0.89 mol) in water (1.25 l) was heated to reflux over 1.75 hours and maintained at reflux until all the permangante was consumed (2 hours). The mixture was filtered hot through Celite, and the filter pad was washed with hot water (200ml). The filtrate was acidified with glacial acetic acid (58.75 ml), and reduced to a volume of 300ml. The filtrate was then continuously extracted with dichloromethane (redistilled , 350ml). The DCM extracts were dried (anhydrous $MgSO_4$) and rotor-evaporated to dryness to provide a white solid.

Recrystallisation from ethyl acetate afforded the white crystals of 2-phenyl-3-pyridine carboxylic acid in 87% yield, with a m.p. 166-8°C (Lit[24] 166-8°C). TLC.,Rf 0.02 , Infrared ν C=O 1710 cm^{-1}, $M^{+\cdot}$ 199 (appendix I.26) ; proton NMR (appendix II.1) ; 13-C NMR (appendix III.3).

5H-Indeno[1,2-b]pyridine-5-one (8)

The cyclisation of 2-phenyl-3-pyridine carboxylic acid (158) was carried out using the method of DuPriest et al[24].

A mixture of (158), (5.0g , 0.025mol) and polyphosphoric acid (83.33g) was heated over 20 minutes to 225°C and maintained at 210-215°C for 2 hours, after which the hot solution was poured into 3M NaOH (417 ml).Some additional NaOH was added to make the solution basic. The mixture was cooled in ice and the solid that precipitated out was

collected by filtration and dried.

Recrystallisation from toluene afforded the yellow crystals of 5H-indeno[1,2-b]pyridine-5-one (8) in 97% yield, with a m.p. 140-1°C (Lit[24] 140-1°C). T L C ,Rf 0.23, Infrared ν C=O 1724 cm^{-1}, $M^{+\bullet}$ 181 (appendix I.27); proton NMR (appendix II.3) ; 13-C NMR (appendix III.2). Found C, 79.59 ; H, 3.62 ; N, 7.67 %. $C_{12}H_7NO$ requires C, 79.56 ; H, 3.87 ; N, 7.73 %.

(RS)5-Hydroxy-5H-indeno[1,2-b]pyridine (208)

5H-Indeno[1,2-b]pyridine-5-one (8),(2.5g ; 13.8 mmol) was dissolved in propan-2-ol (100ml) and THF (15ml). The solution was stirred at 60-70°C and sodium borohydride (0.3g) was then added as a slurry in THF (9.5ml).The reaction mixture was stirred at 60°C for 2.5 hours and then the excess solvent was removed and the mixture was poured onto ice/ water (125ml). After 1 hour, the solid that had separated out was collected and washed with diethyl ether. Recrystallisation from toluene/methanol ,afforded (RS)5-hydroxy-5H-indeno[1,2-b]pyridine (208) in 83% yield, which had a m.p. 150-2°C (Lit[77] 150-2°C). T L C ,Rf 0.26 ; Infrared ν OH 3450 , 3575 cm^{-1}, $M^{+\bullet}$ 183 (appendix I.28); proton NMR (appendix II.4) ; 13-C NMR (appendix III.5).

5H-Indeno[1,2-b]pyridine-5-one hydrazone (55)

Following the method of Mlochowski and Szulc[32], a mixture of 5H-indeno[1,2-b]pyridine-5-one (8), (453mg ; 2.5 mmol), glacial acetic acid (0.15 ml ; 2.5mmol), methanol (5ml) and hydrazine hydrate (0.78ml ; 15.5 mmol, 80%) were heated under reflux for one hour. The solution was evaporated under

reduced pressure, the residue was then washed with water, filtered and dried. Recrystallisation from chloroform afforded the fawn crystals of the hydrazone, in 78% yield, with a m.p. 153-4°C (Lit[32] 153-4°C), T L C ,Rf 0.48 ; Infrared ν C=N 1581 , NH 1404 cm^{-1}, $M^{+\cdot}$ 195 (appendix I.29), proton NMR (appendix II.5); 13-C NMR (appendix III.4).

Attempted reduction of 5H-indeno[1,2-b]pyridine-5-one (8) using Huang-Minlon modification of the Wolff-Kishner reduction[103].

The ketone (8) , (4.55g ; 25 mmol), triethylene glycol (25ml) and potassium hydroxide (3.25g) were placed in a RBF. Hydrazine hydrate (5ml ;85%) was added and the mixture was refluxed for 45 minutes.

The condenser was removed and equiped for distillation. The low-boiling material (112°C) was distilled off until the temperature rose to 175-80°C.The reflux condenser was re-fitted and the solution was heated under reflux for 3 hours.The aqueous distillate was combined with the reaction mixture (black in colour), and was extracted with diethyl ether (3 x 10ml) which also turned black in colour. Separate layers could not be seen.The ether later was removed by pipette from the top of the separating funnel, and was washed with water to remove any untreated hydrazine. The ether layer was rotor-evaporated to dryness to afford a pale fawn solid, recrystallisation from toluene/methanol gave white cystals of the unexpected alcohol : (RS)-5-hydroxy-5H-indeno[1,2-b]pyridine (208) in 20% yield,which had m.p. 150-2°C (Lit[77] 150-2°C), T L C ,Rf 0.27 ; Infrared ν OH 3568 , 3148 cm^{-1}; $M^{+\cdot}$ 183 (appendix I.28) ; proton NMR (appendix II.4);13-C NMR (appendix III.5).

The attempted reduction of 5H-indeno[1,2-b]pyridine-5-one (8) using triethylsilane (TES)[104].

5H-Indeno[1,2-b]pyridine-5-one (8), (100mg;0.55mmol) was dissolved in trifluoroacetic acid (624mg ;0.54mmol) and tetrachloromethane (1ml) in a RBF. At 45°C , TES (140mg ; 1.19 mmol) was added over 15 minutes.. After twentyfour hours , the solution was cooled and saturated sodium hydrogen carbonate (5ml) was added.The mixture was extracted with ethyl acetate (3 x 5 ml) and the extracts were dried. The combined extracts were rotor-evaporated to dryness leaving a pale yellow solid, which was collected and dried.

The solid had a m.p. 139-141°C which remained unchanged on admixture with authentic 5H-indeno[1,2-b]pyridine-5-one (8). The starting ketone was recovered in 56% yield.

Repetition of the above experiment gave the starting material recovered in 78% yield.

The attempted reduction of fluorenone (216) using TES[104].

Fluorenone (2.0g ; 11mmol) was dissolved in trifluoroacetic acid (12.48g ; 10.8mmol) and tetrachloromethane (1 ml). TES (2.8g ; 23.8 mmol) was added over 15 minutes, after addition was complete, the solution was stirred at 45°C for 24 hours.After cooling , a pink precipitate was obtained which did not dissolve on addition of saturated sodium hydrogen carbonate (100ml). The precipitate was removed by filtration and recrystallised from ethanol to afford the white crystals of 9,9'-bifluorenyl (77%) which had m.p. 246°C (Lit[105] 246°C); T.L.C ,Rf 0.77 ; Infrared ν C-H str 3014 , 3037 , ν C=C str 1448 cm^{-1}; $M^{+\bullet}$ 330 (appendix I.30);

proton NMR (appendix II.6).

5H-Indeno[1,2-b]pyridine (4)

Following the method of Chatterjea and Prasad[46], 5H-indeno[1,2-b]pyridine-5-one (0.4g ; 2.2mmol) and red phosphorus (0.8g) were refluxed together in hydroiodic acid (20ml) for 7 hours. After this time the reaction was stopped and cooled, white needles of the hydroiodide of 5H-indeno[1,2-b]pyridine-5-one separated out.
The crystals together with unreacted phosphorus were collected and dissolved in hot water (the red phosphorus which did not dissolve was collected by filtration).
The aqueous solution was made alkaline with NaOH (6ml, 6M) and white crystals appeared. The solution was cooled on an ice-bath and the crystals were collected and dried.
Recrystallisation from ether afforded pure 5H-indeno[1,2-b]-pyridine (4), (78%) which had m.p. 93-5°C (Lit[46] 93-5°C) ; T L C ,Rf 0.17 ; Infrared νN-H 3399 ,νC-H str 3037 ,2998 cm^{-1}(aromatic) ,νC=C str 1567 cm^{-1}; $M^{+\bullet}$ 167 (appendix I.31) proton NMR (appendix II.2) ; 13-C NMR (appendix III.1).

Following the method of DuPriest et al[24], 5H-indeno[1,2-b]pyridine (8), (2.5g ; 14mmol) and hydrazine hydrate (2.7 ml) in diethyene glycol (90ml) was heated to 180°C and maintained at this temperature for 4 hours.
After cooling to room temperature, the mixture was poured into water (250ml) and brine (50ml) and extracted with ethyl acetate (3 x 50ml). The combined extracts were washed with water (2 x 50ml), dried and concentrated to leave a solid product. Recrystallisation (ether) afforded

pure 5H-indeno[1,2-b]pyridine (89%) with m.p. 93-5°C, (Lit[24] 93-5°C); T L C ,Rf 0.17 ; Infrared ν N-H 3399 , C-H str 3037 , 2998 ,ν C=C str 1567 cm^{-1}; M^{+} 167 (appendix I.31); proton NMR (appendix II.2); 13-c NMR (appendix III.1).

Attempted preparation of 5-hydroxy-5-propyl-indeno[1,2-b]-pyridine (218).

All the apparatus was dried at >120°C.Diethyl ether was also dried (Na wire).The magnesium strip was scraped and washed in dry ether and transferred to an oven at 120°C for 30 minutes.The apparatus was 'set-up' hot and under dry nitrogen.These were the standard precautions taken before any Grignard reaction was carried out.

Magnesium turnings (140mg ; 5.7mmol) were placed in a RBF containing ether (10ml) and a magnetic flea. The solution was stirred rapidly, a crystal of iodine and a few drops of a solution of bromopropane (615mg in diethyl ether (10ml)) were added to initiate Grignard formation.Once started (cloudy precipitate), the remaining bromopropane solution was added and the solution was refluxed until all the magnesium had been consumed. The reaction mixture was then cooled on an ice-bath, and a solution of 5H-indeno[1,2-b]-pyridine-5-one (750mg ; 4 mmol) in ether (20ml) was added. The solution, which turned vivid pink in colour, was gently refluxed for 4 hours. The solution was then cooled; ice-water (10ml) and saturated ammonium chloride (10ml) were added to the mixture, which turned to a clear orange colour.The aqueous layer was removed and washed with ether (3 x 15ml).

The ether extracts were combined and dried, the solution was rotor-evaporated to leave a sticky solid, which was redissolved in ethanol and rotor-evaporated to dryness. The solid was dried and recrystallised from toluene to give the starting material in 53 % yield. The solid had m.p. 141-2°C which remained unchanged when mixed with authentic material. Infrared ; ν C=O 1724 cm^{-1} ; T L C ,Rf 0.25 .

This experiment was repeated several times. As well as the standard precautions being stictly adhered to, the 1-bromopropane was redistilled before each use (bp 69-72°C), and the starting ketone (8) was recrystallised twice from toluene.

In each case , the starting ketone (8) was recovered in yields between 50 - 70%.

Preparation of 9-hydroxy-9-propylfluorene (219)

Standard precautions were taken before the reaction commenced. The procedure was identical to that above except the ketone ,fluorenone (216) (1.8g ; 10mmol) was used. The amounts of magnesium turnings and bromopropane were altered accordingly.

The reaction time was extended to 21 hours.

T L C of the crude product indicated five products including the starting material. Repeated flash chromatography, using eluent 80% petroleum spirit (40-60)/ 20% diethyl ether , gave the desired alcohol and some starting material.Recrystallisation from petroleum spirit (40-60°C) afforded a pale yellow solid. Mass spectrometry & infrared examination of this solid indicated the presence of both the desired alcohol and the starting material.

Further flash chromatography gave a small amount of the desired alcohol and 60% recovery of the starting ketone (216). The alcohol: 9-hydroxy-9-propylfluorene was obtained in poor yield (5%) and had m.p. 110-112°C ; T L C ,Rf 0.58 ; Infrared ν OH 3306 cm^{-1}; $M^{+\bullet}$ 224 (appendix I.32) ; proton NMR (appendix II.7).Found: C, 85.67 ; H, 7.17 %.
$C_{16}H_{16}O$ requires C, 85.72 ; H , 7.14 %.

Preparation of 9-butyl-9-hydroxyfluorene (219).

The standard Grignard reaction method was followed. Fluorenone (216),(1.8g ; 10mmol) and bromobutane (1.5g ; 11mmol) were used. Recrystallisation of the final product from toluene afforded a small amount of the desired alcohol (2%), which had m.p. 106 - 8°C ; T L C,Rf 0.51 ; Infrared ν OH 3336 cm^{-1}; $M^{+\bullet}$ 238 (appendix I.33).There was insufficient sample for NMR and elemental analyses.

Attempted preparation of 5-butyl-5-hydroxy-indeno[1,2-b]-pyridine (220).

This experiment followed the general Grignard conditions. 5H-indeno[1,2-b]pyridine-5-one (1.0g ; 5.5mmol) and bromobutane (756mg ; 5.5mmol) were used.
The reaction was 'worked-up' as before and rotorevaporation afforded a sticky orange solid.
The solid was dissolved in DCM and preabsorbed onto silica and placed on a silica column ready for flash chromatography.Elution with petroleum spirit (bp 40-60°C) 55% / ethyl acetate 45% , gave a sample containing both the desired alcohol and some starting material.
Recrystallisation from ethanol gave 20% recovery of the

starting material (mp 140-2°C.Lit[77] 140-2°C); Infrared ν C=O 1724 cm^{-1}.

Rotor-evaporation to dryness of the filtrate gave the alcohol still contaminated with starting material, as indicated by mass spectral examination (appendix I.33i).

Separation of fluorenone (216) and 9-hydroxyfluorene using Girards-T reagent.

Fluorenone (2.0g) and 9-hydroxyfluorene (2.0g) were dissolved in ethanol containing 10; acetic acid (45ml) and were heated for 1 hour with Girards-T reagent (4.5g) in slight excess (giving a 10% soltion of the reagent.)
The cooled solution was diluted with water containing enough alkali (10.8ml ; 6M NaOH) to neutralise 90% of the acid and to give an alcohol content of 20% (180ml of water was added).A solid immediately separated out ,the hydrazone derivative, and was collected.The filtrate was exhaustively extracted with ether to remove non-ketonic compounds ie., the desired alcohol.

The ether fractions were collected and dried.Rotor-evaporation to dryness afforded a pale yellow solid which proved to be the desired alcohol, 9-hydroxyfluorene (by T L C with authentic material), in 90% yield.

Attempted separation of (8) and 5-butyl-5-hydroxy-indeno-[1,2-b]pyridine (220)

The orange solid obtained, when the reaction between (8) and bromobutane was worked-up,was treated with Girards-T.

After heating for 1 hour, the cooled solution afforded a solid which was collected by filtration. By comparison of melting points this solid proved to be unreacted Girards-T reagent (mp 188-192°C).

On addition of alkali to the filtrate, a second solid separated out which proved by T L C and Infrared examination to be a mixture of the starting ketone (8) and the desired alcohol. The resulting filtrate (obtained after removal of the second solid) was extracted with ether. Rotor-evaporation of the combined fractions gave a third solid, which by T L C and Infrared examination proved to be a mixture of the starting ketone (8) and the alcohol (220). (ν C=O 1715 cm^{-1}, ν OH 3305 cm^{-1}.)

9-Hydroxy-9-phenylfluorene (223).

The Grignard reaction between fluorenone (1.0g ; 5.5mmol) and bromobenzene (0.444g) was carried out using the standard method, except THF was used as solvent.

Work-up of the resulting solution afforded a solid, which when recrystallised from ethanol afforded the desired alcohol : 9-hydroxy-9-phenylfluorene (57%), which had m.p. 106 -7°C (Lit[105] 106-7°C); Infrared ν OH 3399 cm^{-1} ; $M^{+\cdot}$ 258 (appendix (I.34) : T L C ,Rf 0.47.

5-Hydroxy-5-phenylindeno[1,2-b]pyridine (222)

The above experiment was repeated using the ketone (8) , (1.0g ; 5.5 mmol). A yellow solid was obtained after rotor-evaporation which had several products, as evidenced by T L C examination.

Purification , several times , by flash chromatography with eluent petroleum spirit (bp 60-80°C) 50% / ethyl acetate 50%, gave a resulting solid which contained both the alcohol (222) and the starting material (8) which could not be separated.

The experiment was repeated, except reflux was continued for 10 hours. Work-up and attempted purification by flash chromatography gave the same result.

The above experiment was repeated using the solvent THF, instead of ether. Again, work-up and purification by flash chromatography gave similar results.

In the above experiments, the product finally obtained proved to be a mixture of the starting material and desired alcohol (222).These could not be separated sufficiently to give good results by purification using flash chromatography , as the Rf values were very close together .

It was found, on preparing a sample for T L C , that the pure ketone dissolved in DCM whereas the alcohol did not. Thus purely by a difference in solubility, the pure alcohol was obtained.

5-Hydroxy-5-phenylindeno[1,2-b]pyridine (222) was obtained in 35% yield in the first experiment.Increasing the reaction time increased the yield to 53%.Changing the solvent to THF gave the alcohol in 50% yield.

The alcohol (222) had m.p. 218-220°C ; T L C ,Rf 0.25; Infrared ν_{OH} 3138 cm^{-1} ; $M^{+\cdot}$ 259 (appendix I.35) ; proton NMR (appendix II.8) ; 13-C NMR (appendix III.6). Found : C 82.94 ; H,5.22 ;N,5.64%.$C_{18}H_{13}NO$ requires C 83.40 ; H 5.02 ; N, 5.40% .

5H-Indeno[1,2-b]pyridine-5-one oxime (224)

The oxime was prepared using the method of Harwood and Moody.[109] 5H-indeno[1,2-b]pyridine-5-one (1.18g ;6.5mmol) was dissolved in ethanol (20ml).To this was added hydroxylamine hydrochloride (1.22g ; 17.5 mmol) and sodium acetate trihydrate (2.38g ;17.5mmol) were dissolved in warm water (15ml). The mixture was refluxed for 20 minutes and the hot solution was rapidly filtered.The filtrate was cooled on an ice-bath and the crystalline product which separated out was collected and dried.

Recrystallisation from ethanol afforded the cream crystals of 5H-indeno[1,2-b]pyridine oxime in 63% yield. The oxime had a m.p. 244-6°C (Lit[31] 244-5°C) .T.L.C ;Rf 0.13 ; Infrared νOH 3443 cm^{-1} , νC=C ,νC=N 1594 , 1575 cm^{-1}, $M^{+\cdot}$ 196, (Appendix I. 36); proton NMR (Appendix II. 9) ; 13-C NMR (Appendix III. 7).

5H-Indeno[1,2-b]pyridine-5-one 4-chlorobenzyloxime.(225).

The experiment was carried out as for the above oxime except 4-chlorobenylamine hydrochloride (2.2g ; 9.625mmol) was used and the reaction mixture was refluxed for 30 minutes. Recrystallisation of the resulting solid precipitate afforded 5H-indeno[1,2-b] pyridine-5-one 4-chlorobenzyloxime in 68% yield, which had a m.p. 96-7°C. T.L.C ;Rf 0.62 ; Infrared νC=C,C=N 1608 , 1581 cm^{-1} ; $M^{+\cdot}$ 320 (Appendix I. 37), proton NMR (Appendix II. 10), 13-C NMR (Appendix III. 8). Found : C, 64.47% ; H, 8.73 % ; N, 4.24 %. $C_{19}H_{13}N_2OCl$ requires C 71.25% , H 4.06 % , N 8.75 % .

5H-Indeno [1,2-b] pyridine-5-one 2,4-dichlorobenzyloxime (226).

The oxime was prepared according to the above method except 2,4-dichlorobenzylamine hydrochloride (1.86g ; 9.625mmol) was used. After 30 minutes the hot solution was filtered and the filtrate was cooled in an ice-bath. The crystals which separated out were collected and dried. Recrystallisation from ethanol afforded 5H-indeno [1,2-b] pyridine-5-one 2,4-dichlorobenzyloxime in 91% yield, with a m.p. 118-120°C. T L C ; Rf 0.66 ; Infrared ν C=C,C=N 1591, 1566 cm^{-1}; $M^{+\cdot}$ 354 (Appendix I.38); proton NMR (Appendix II.11); 13-C NMR (Appendix III. 9). Found :C 62.81% ; H 3.55% ; N 7.86 % . $C_{19}H_{12}N_2OCl_2$ requires C 64.41 % , H 3.39% , N 7.91%.

9-Fluorenone oxime (227)

The oxime was prepared using the method of Harwood and Moody[109]. 9-fluorenone (1.0g ; 5.5mmol) was dissolved in ethanol (20ml). To this was added hydroxylamine hydrochloride (0.67g ; 9.6mmol) and sodium acetate trihydrate (0.75g ; 5.5mmol) dissolved in warm water (15ml). After refluxing for 20 minutes, the hot solution was filtered, the filtrate being cooled in an ice-bath, The solid which separated out was collected and dried. Recrystallisation from ethanol afforded 9-fluorenone oxime in 84% yield, which had a m.p. 196-7°C, (lit[103] 196-7°C); T L C ; Rf 0.17 ; Infrared ν OH 3400 cm^{-1}; $M^{+\cdot}$ 195 (Appendix I.39); proton NMR (Appendix II.12).

6-Phenanthridone (228).

Based on a method of Vogel,[103] 9-fluorenone oxime (2.0g ; 10.25 mmol) was added to polyphosphoric acid (60g).The reaction mixture was stirred at 175°C for 15 minutes.The solution was cooled to 80°C and then stirred into cold water (300ml).The solid which separated out was filtered, washed (cold water, 3 x 50ml) and dried at 100°C. Recrystallisation from ethanol afforded 6-phenanthridone , 83% yield, with a m.p. 290-2°C, Lit 290-2°C:[103] T L C ;Rf 0.42 ; Infrared Amide I & II,1650 ,1665. ∂NH 3200 , ∂C=O 1680 cm^{-1}. $M^{+\cdot}$ 195 (appendix I. 40).

Attempted Beckmann rearrangement of 5H-indeno[1,2-b]pyridine-5-one oxime (224).

a) To polyphosphoric acid (10g) was added the oxime (1.0g ; 5 mmol).The mixture was heated on a boiling water bath for 10 minutes, with continuous stirring.

The mixture was poured onto crushed ice (20g) and stirred. However, no amide precipitation was observed. The solution was made basic with NaOH to pH 7 and a white presipitate appeared which was collected and dried.

The solid had a m.p. of > 340°C ; Infrared ∂C=O 1636 , ∂N-H 3200 cm^{-1}.No amide I & II absorptions.$M^{+\cdot}$ 196 (appendix I.41).

b)the above experiment was repeated at higher temperatures of 120°C and 180°C (oil bath) for 20 minutes. In both cases the starting oxime (224) was recovered in approximately 60% yield, as confirmed by m.p. (no change on admixture with authentic oxime) and Infrared ∂OH 3443 ,∂C=C , ∂C=N ,1594 , 1575 cm^{-1}.

c)the above experiment was repeated at 120°C for extended periods of time, namely 30 minutes and 1 hour.
In each case the starting oxime (224) was recovered in approximately 70% yield, as confirmed by m.p. and infrared.

5-Acetamido-5H-indeno[1,2-b]pyridine(230)

Using the method of Petrow et al[28], 5H-indeno[1,2-b]pyridine-5-one oxime (224),(350mg ; 1.78mmol),anhydrous sodium acetate (350mg) in acetic anhydride (3.5g) was treated with zinc dust (700mg) added portionwise. After addition was complete, the mixture was heated under reflux for 1 hour, filtered hot and the filtrate was poured into ice-water (16ml).The solution was made alkaline (aq NaOH) and the precipitate which separated out was collected and dried.Recrystallisation from ethyl acetate afforded the pure amide : 5-Acetamido-5H-indeno[1,2-b]-pyridine (64%),which had m.p. 238-40°C ; T L C ,Rf 0.42 ; Infrared ν N-H 3265 , Amide I,II 1643 , 1542 cm^{-1}.$M^{+\cdot}$224 (appendix I.53); proton NMR (appendix II.13); 13-C (appendix III.10).Found: C 75.27 ; H, 5.39 ; N, 12.75%. $C_{14}H_{12}N_2O$ requires C, 75.00 ; H, 5.36 ; N, 14.28 %.

2,4-DNP derivative of 5H-indeno[1,2-b]pyridine-5-one (231).

2,4-dinitrohydrazine (0.25g) was suspended in methanol(5ml) and concentrated H_2SO_4 (0.45ml) was added cautiously. The warm solution was filtered and a solution of the ketone (8), (0.15g; 0.8mmol) in methanol (2 ml) was added.The solution was cooled and a bright orange precipitate separated out,which was washed with cold methanol and dried.Recrystallisation from ethanol afforded 5H-indeno[1,2-b]pyridin-5-one 2,4-dinitrophenyl-hydrazone (60%), with m.p. 262-4°C ; T L C ,Rf 0.54 ;

Infrared N-H str 3436 ,δN-O str 1616 , 1499 cm^{-1} ; $M^{+\cdot}$ 361 (appendix I.54).

7-Bromo-5H-indeno[1,2-b]pyridine-5-one(233)

Following the method of Mlochowski and Szulc[15], to a solution of 5H-indeno[1,2-b]pyridine-5-one (0.91g ;5 mmol)in H_2SO_4 (75ml ,70% v/v) heated to 45-50°C was added NBS (5 mmol) portionwise over 30 minutes. Vigorous stirring was maintained throughout addition and for a further hour whilst the temperature was maintained at 45-50°C.The reaction mixture was poured into water (200ml) and made alkaline with aq NH_3. The solid which precipitated out was collected and dried. Recrystallisation from ethanol afforded (233) in 85% yield, which had m.p. 157-9°C (Lit[15]158-9°C); T L C ,Rf 0.76 ; Infrared δC=O 1717 cm^{-1} ; $M^{+\cdot}$259/261 (appendix I.42) ; proton NMR (appendix II.14): 13-C NMR (appendix III.11).

7,9-Dibromo-5H-indeno[1,2-b]pyridine-5-one (234).

The method is the same as above except that a 2:1 ratio between the NBS and the ketone (8) was used . NBS(5 mmol) was added with vigorous stirring to the ketone (8), (2.5mmol), following the method of Mlochowski and Szulc[15]. Recrystallisation from ethanol afforded the dibromo- compound (234) in 48% yield,with m.p. 210-12°C (Lit[15]211-2°C); T L C , Rf 0.94 ; Infrared δC=O 1722 cm^{-1} ; $M^{+\cdot}$337/339/341 (appendix I.43); proton NMR (appendix II.15); 13-C NMR (appendix II.12).

Dibromo- and Tribromo-5H-indeno[1,2-b]pyridine (235,236).

Using a similar method to that above, 5H-indeno[1,2-b]-pyridine (4) was reacted with NBS in a 1:1 ratio. A sticky solid was collected which could not be purified by TLC. Dissolution in DCM provided a sample for mass spectral examination which indicated the presence of a dibromo- compound (235), (appendix I.44).

When (4) was reacted with NBS in a 1:2 ratio , a sticky solid was again collected, which could not be purified by TLC. Mass spectral examination indicated the presence of a tribromo- compound (236),(appendix I.45).

Further bromination of 5H-indeno[1,2-b]pyridine (237)

5H-Indeno[1,2-b]pyridine (0.5g ;2.99mmol) was dissolved in a solution of 70% v/v H_2SO_4 (75ml), heated to 45-50°C.To this was added NBS (1.86g ; 3.5 mol excess) over 30 minutes with vigorous stirring. The solution was heated at this temperature for 1 hour.The reaction mixture was poured into water (200ml) and made alkaline (aq NH_3).The solid precipitate was collected and dried recrystallisation from ether afforded 6,7,8,9-tetrabromo-5H-indeno[1,2-b]pyridine in 62% yield with a m.p. 209-211°C. T L C ,Rf 0.45 ; $M^{+\bullet}$479/481/483/485 (appendix I.46); proton NMR (appendix II.16); 13-C NMR (appendix III.13),(appendix III.14).Found C,33.15 ; N, 3.02 ; Br 59.37%. $C_{12}H_5NBr_4$ requires C 30.06 ; N, 2.93 ; Br 65.97 %.

7-Nitro-5H-indeno[1,2-b]pyridine-5-one (238).

Following the method of Petrow[12]. 5H-Indeno[1,2-b]pyridine-5-one (420mg ; 2.3mmol) was dissolved in sulphuric acid (2.5ml) Maintaining the temperature at 0°C, potassium nitrate (250mg) was slowly added.

Once addition was complete, the mixture was returned to ordinary temperature (room temp.) and was heated on a boiling water bath (73°C) for 1 hour.

The solution was cooled and poured onto ice, then made alkaline with ammonia. The precipitate obtained was recrystallised from ethanol to afford 7-nitro-5H-indeno-[1,2-b]pyridine-5-one in 78% yield, with a m.p. 174-6°C. T L C ; Rf 0.55 ; Infrared νC=O 1726 cm^{-1}, νNO_2 1583 , 1533 cm^{-1} ; $M^{+\cdot}$ 226 (Appendix I.47), proton NMR (Appendix II.17) 13-C NMR (Appendix III.15). Found C,63.39 %; H,2.65% ; N, 12.14%. $C_{12}H_6N_2O_3$ requires C 63.72% ; H, 2.65 % ; N, 12.39%

7-Nitro-5H-indeno[1,2-b]pyridine (239).

5H-Indeno[1,2-b]pyridine (0.5g , 2.99mmol) was dissolved in sulphuric acid (3.25ml) and treated as above.(At 0°C , potassium nitrate (0.325g) was slowly added portionwise). When the solution was cooled and made alkaline, purple crystals immediately separated out. Recrystallisation from dichloromethane afforded pure 7-nitro-5H-indeno[1,2-b]pyridine in 61.5% yield, with a m.p. 144-6°C. T L C ; Rf 0.47 ; Infrared νNO_2 1522 , 1342 cm^{-1} ; $M^{+\cdot}$ 212 (Appendix I.48) proton NMR (Appendix II.18),13C NMR (appendix III.16) Found ,C,67.34%; H,3.45 % N,13.28 %. $C_{12}H_8N_2O_2$ requires : C 67.93% ; H, 3.77% ; N, 13.21 %.

Attempted reduction of 7-nitro-5H-indeno [1,2-b] pyridine-5-one

Attempts were made to reduce (238) following the method of DuPriest et al [24].

7-Nitro-5H-indeno [1,2-b] pyridine-5-one (0.75g ; 4.14mmol) and hydrazine monohydrate (0.9ml) in digol (30ml) were heated with stirring to 180°C and maintained at this temperature for four hours.

After cooling to room temperature, the mixture was poured into cold water (90ml) and brine (20ml) and extracted with ethyl acetate (3 x 20ml).

The combined extracts were washed with water (3 x 20ml), dried and concentrated to leave a solid product which on recrystallisation from toluene afforded the novel compound : 7-amino-5H-indeno [1,2-b] pyridine in 69% yield, with a m.p. 178°C; T L C ;Rf 0.37 ; Infrared δNH_2 3458 , 3315 , 3191 cm^{-1}; $M^{+\cdot}$ 182 (Appendix I.49), proton NMR (Appendix II.19), Found: C, 79.83 ; H, 5.95 ; N, 14.20 % . $C_{12}H_{10}N_2$ requires C,79.12 ; H, 5.49 ; N, 15.39 %.

Clemmensen reduction of 7-nitro-5H-indeno [1,2-b] pyridine-5-one (238) to 7-nitro-5H-indeno [1,2-b] pyridine (239)

Following the method of Harwood and Moody [109], zinc wool (2.768g ; 0.05 mol) was cut up and introduced into a RBF. Mercury (II) chloride (0.11g ; 0.4mmol) was dissolved in a mixture of concentrated hydrochloric acid (0.1ml) and water (2 ml) and then added to the zinc wool in the flask.

The flask was swirled for 5 minutes and the aqueous supernatant liquid was decanted from the zinc amalgam.

The amalgam was immediately covered with a mixture of conc. HCl (5ml) and water (1ml). 7-Nitro-5H-indeno[1,2-b]pyridine-5-one (0.904g ; 4 mmol) was added to the flask and refluxed for 2 hours. At 30 minute intervals during the reflux period, a further 0.2 ml of c.HCl was added down the condenser. After 2 hours, the mixture was cooled and basified with NaOH. Ether (5ml) was added and the resulting solution was transferred to a separating funnel. The organic layer was separated and the aqueous layer was extracted with ether (3 x 5 ml). The combined ether extracts were washed with water (2 x 5ml) and dried ($MgSO_4$). Recrystallisation from dichloromethane afforded 7-nitro-5H-indeno[1,2-b]pyridine (239) in 35% yield, with m.p. 144-6°C; T L C , Rf 0.46 ; Infrared νNO_2 1522 , 1341 cm^{-1} ; $M^{+\cdot}$ 212 (appendix I.48) , proton NMR (appendix II.18) ; 13-C NMR (appendix III.16). Found C, 67.34 ; H, 3.45 ; N, 13.28%. $C_{12}H_8N_2O_2$ requires C 67.93 ; H, 3.77 ; N 13.21 %.

7-Amino-5H-indeno[1,2-b]pyridine - 5-one (241)

Following the method of Vogel[103], crystallised sodium sulphide $Na_2S.9H_2O$, (18.0g ; 75mmol) was dissolved in water (50ml); finely powdered sodium hydrogen carbonate (6.0g ; 71.4 mmol) was added in small portions with continuous stirring. When the carbonate had completely dissolved, methanol (50ml) was added and the solution was cooled to below 20°C. The precipitated sodium carbonate was filtered off and washed with methanol (3 x 8ml). The filtrate and the washings were retained and used immediately for the reduction of the nitro compound (238)

7-Nitro-5H-indeno[1,2-b]pyridine-5-one (0.5g ; 2.2mmol) was dissolved in methanol (50ml).With shaking, the previously prepared methanolic solution of sodium hydrogen sulphide was added (40ml) and the mixture was refluxed for 20 minutes.The solution was cooled and the excess of methanol was removed by rotor-evaporation to afford a red solid in 83% yield. 7-amino-5H-indeno[1,2-b]pyridine-5-one had m.p. 185-7°C ; T L C ,Rf 0.42 ; Infrared νC=O 1718 , νNH_2 3351 cm^{-1}; $M^{+\cdot}$ 196 (appendix I.50); proton NMR (appendix II.20) , 13-C NMR (appendix III.17). Found: C 71.93 ; H, 3.50 ; N, 13.78%. $C_{12}H_6N_2O$ requires C 73.47 ;H, 4.08 ; N, 14.28%.

7-Hydroxy-5H-indeno[1,2-b]pyridine-5-one (242)

Using the method of Vogel[103], 7-amino-5H-indeno[1,2-b]pyridine-5-one (0.5g ; 2.5mmol) was dissolved in 1:1 sulphuric acid : water (3ml) and iced water (9ml) with stirring. The solution was cooled to 0-5°C and sodium nitrate (0.18g ;26 mmol) in water (5ml) was added over 10 minutes until a permanent colour was immediately given to KI-starch paper. Whilst diazotisation was in progress; 1:1 sulphuric acid:water (4ml) was heated to boiling. The diazotised solution was added over 30 minutes. After addition the mixture was boiled for a further 5 minutes and cooled. NaOH(40%) was added to neutralise the acid. After leaving in a fridge, a fawn solid was obtained by filtration. Recrystallisation from toluene afforded the pure phenol (242), in 19% yield,which had m.p. 194-6°C. T L C , Rf 0.72 ; Infrared. νC=O 1720 , νOH 1250 ,1400 cm^{-1}. $M^{+\cdot}$ 197 (appendix I.51) ; proton NMR (appendix II.21). Found: C 73.31; H 3.53 ; N, 6.93%. $C_{12}H_7NO$ requires C 73.10 ; H 3.55 ; N 7.11%.

7-Hydroxy-5H-indeno[1,2-b]pyridine (243)

The experimental method was identical to that above except 7-amino-5H-indeno[1,2-b]pyridine was used as starting material. Addition of NaOH(40%) to the reaction solution afforded a pale fawn solid. Recrystallisation from toluene afforded a yellow solid, which had m.p. 243-5°C; T L C , Rf 0.64 ; Infrared ν OH 3382 , 1269 cm^{-1}; $M^{+\cdot}$ 183 (appendix I.52) ; proton NMR (appendix II.22). Found: C 78.65 ; H 4.83 ; N 7.54 %. $C_{12}H_9NO$ requires C 78.69 ; H, 4.92 ; N 7.65 %. Yield - 27%.

7-Bromo-5H-indeno[1,2-b]pyridine-5-one oxime (244)

7-Bromo-5H-indeno[1,2-b] pyridine-5-one (0.5g ; 1.93 mmol) was dissolved in ethanol (45ml) and refluxed. To this solution was added hydroxylamine hydrochloride (1.0g ; 14.4mmol) and sodium acetate trihydrate (2.0g ; 24.4mmol) dissolved in warm water (30ml). The mixture was refluxed for 1.5 hours and the solution was filtered hot and then cooled in an ice-bath. A white precipitate separated out and was collected and dried. Recrystallisation from ethanol afforded the oxime in 85% yield, which had m.p. 266-7°C. T L C , Rf 0.42 ; Infrared N-OH 3450 cm^{-1}, ν C=N 1580 , N-O 955 , 1000 cm^{-1}; $M^{+\cdot}$ 274/276 (appendix I.55) , proton NMR (appendix II.23). Found: C 51.42 , H 2.24 , N 9.86% $C_{12}H_7N_2OBr$ requires C 52.56 , H 2.55 , N 10.22%.

7-Nitro-5H-indeno[1,2-b]pyridine-5-one oxime (245)

The method is similar to the previous experiment except 7-nitro-5H-indeno[1,2-b]pyridine-5-one (0.44g ; 1.93 mmol) was used. The precipitate finally obtained was recrystallised from ethanol to give 7-nitro-5H-indeno[1,2-b]pyridine-5-one oxime in 99% yield, with a m.p. 302-3°C. T L C , Rf 0.36 ; Infrared ν C=N 1590 , ν N-O 970 , 1018 cm^{-1}, ν N-OH 3100 cm^{-1}. $M^{+\cdot}$ 241 (appendix I.56), proton NMR (appendix II.24). Found: C 59.26 , H 2.31 , N 15.51%. $C_{12}H_7N_3O_3$ requires C 59.75 ,

H 2.90 ; N 17.43 %.

5,7-Diacetamido-5H-indeno[1,2-b]pyridine (246)

7-Nitro-5H-indeno[1,2-b]pyridine-5-one oxime (0.5g ; 2mmol), anhydrous sodium acetate (0.5g ; 6 mmol) and acetic anhydride (5.0g ; 49mmol) were treated with zinc dust (1.0g ; 15 mmol), added portion-wise.The mixture was heated under reflux for 1 hour, filtered hot and the filtrate was poured into ice-water (24ml).The solution was made alkaline (aq NaOH).On cooling a yellow precipitate separated out which was collected and dried. Recrystallisation from chloroform gave 5,7-diacetamdio-5H-indeno[1,2-b]pyridine (246) in 93% yield, which had m.p. 213-4°C. T L C ,Rf 0.56 ; Infrared νC=O 1650, N-H 3270 , amide I,II 1415 , 1560 cm^{-1}. $M^{+\bullet}$281 (appendix I.57), proton NMR (appendix II.25).Found : C 68.50 ; H 5.16 ;N 12.28%. $C_{16}H_{15}N_3O_2$ requires C 68.33 ; H 5.34 ; N 14.95%.

7-Acetamido-5H-indeno[1,2-b]pyridine (247).

7-Nitro-5H-indeno[1,2-b]pyridine-5-one (500mg ;2.2mmol), anhydrous sodium acetate (500mg) and acetic anhydride (5g) were treated with zinc dust (1.0g) added portionwise, as above. Basification of the final solution gave a fine precipitate which was collected and dried.Recrystallisation from acetone afforded 7-acetamido-5H-indeno[1,2-b]pyridine in 12% yield, which had m.p. 226-7°C. T L C ,Rf 0.47 ; Infrared amide I,II 1690 , 1600 cm^{-1}.$M^{+\bullet}$224 (appendix I.58).Found: C 75.11 ; H 5.09 ; N 12.68% $C_{14}H_{11}N_3O_3$requires C 75.00 ; H 5.36 ; N, 12.50 %.

5-Acetamido-7-nitro-5H-indeno[1,2-b]pyridine (248)

5-acetamido-5H-indeno[1,2-b]pyridine (300mg ; 1.34 mmol) was dissolved in sulphuric acid (2 ml). Maintaining the temperature at 0-5°C, potassium nitrate (200mg) was slowly added. Once addition was complete, the mixture was returned to room temperature and was heated on a boiling water bath for 1 hour. The solution was cooled and poured into ice and made alkaline with aq ammonia. The blue solid which separated out was collected and dried. Recrystallisation from ethanol afforded the white crystals of 5-acetamido-7-nitro-5H-indeno[1,2-b]pyridine (87%), which had m.p. 232-4°C. T L C ,Rf 0.43 ; Infrared Amide I,II 1523 , 1655 ,νNO_2 1442 , 1573 cm^{-1}. $M^{+\bullet}$ 269 (appendix I.59).

5H-Indeno[1,2-b]pyridine-5-one N-oxide (249).

Following the method of Ochiai[110], (8),(1.0g ; 5.5mmol) was dissolved in acetic acid (7ml) in a RBF. Cautiously , to this, was added 30% hydrogen peroxide (0.9ml) with stirring. The solution was heated to 70°C and maintained at this temperature for 18 hours.The excess of solvent was removed and cold water (2ml) was added and the solution was again, rotor-evaporated to dryness.Recrystallisation from aq ethanol gave 5H-indeno[1,2-b]pyridine-5-one N-oxide (75%), which had m.p. 254-6°C (Lit[110] 254-6°C). T L C ,Rf 0.5 ; Infrared ν C=O 1720 ,ν N → O 1280 cm^{-1}. $M^{+\bullet}$ 197 (appendix I.60); proton (appendix II.26); 13-C NMR (appendix III.18). Found C 73.24 ; H 3.49 , N 7.27%. $C_{12}H_7NO_2$ requires C 73.10 ; H 3.55 ; N 7.11 %.

5H-Indeno[1,2-b]pyridine N-oxide (250)

The experimental procedure is identical to that above except 5H-indeno[1,2-b]pyridine (1.0g ; 5.9mmol) was used.The resulting solid was recrystallised from ethyl acetate to afford 5H-indeno[1,2-b]pyridine N-oxide in 30% yield, which had m.p. 162-3°C.T L C ,Rf 0.43 ; Infrared νN→O 1271 ,1235 , 1223 cm^{-1}; $M^{+\cdot}$183 (appendix I.61);proton NMR (appendix II.27). Found: C 78.77 ; H 4.54 ; N 7.89%. $C_{12}H_9NO$ requires C 78.69 ; H 4.92 ; N 7.65 %.

7-Nitro,5H-indeno[1,2-b]pyridine-5-one N-oxide (251)

The method of Ochiai[110] was again used.The method was identical to that used for the previous N-oxide except that 7-nitro,5H-indeno[1,2-b]pyridine-5-one (1.0g; 4.4mmol) was used.
The resulting solid was recrystallised from ethanol to afford the N-oxide (251) in 50% yield,with m.p. 273°C. T L C ,Rf 0.64 ;Infrared νC=O 1732 ,νN→O 1282 cm^{-1} ,νNO_2 1531 , 1351 cm^{-1}. $M^{+\cdot}$242 (appendix I.62); proton NMR(appendix II.28). Found: C 59.45 ; H 3.04 ; N 9.93%. Also C 59.23 ; H 3.21 ; N 9.76 %. $C_{12}H_6N_2O_4$ requires C 59.50 ; H 2.48 ; N 11.50%.

7-Nitro,5H-indeno[1,2-b]pyridine N-oxide (252).

The method is identical to that above except that 7-nitro,5H-indeno[1,2-b]pyridine (1.0g; 4.7mmol) was used.
Recrystallisation from ethanol afforded the N-oxide (252) in 29% yield,which had m.p. 174-5°C.T L C ,Rf 0.43 ; Infrared νNO_2 1526 , 1343 cm^{-1},νN→O 1282 cm^{-1}; $M^{+\cdot}$228 (appendix I.63); proton NMR (appendix II.29).Found: C 62.58 , H 3.53 , N 11.41%. Also 62.69 ; H 3.50 ; N 11.41 %.$C_{12}H_8N_2O_3$ requires C 63.16 ; H 3.51 ; N 12.28%.

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Appendix I

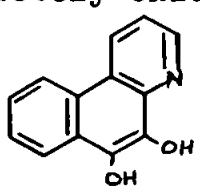
Mass Spectra

Summary of Mass spectra (Appendix I).

During the course of the project the mass spectra of most of the compounds have been recorded.The fragmentation routes of the indenopyridine compounds under electron impact ionisation exhibit similarity dependent on the substituents present.

1.The mass spectra of the indenyl enamides; appendix I.2,3,4,5,8,9 and 10 indicated the presence of the expected fragments. The enamide group (I.2,3,4,5) lost CH_3CO or CH_2CO initially followed by ring cleavage.The dimer compounds lost an 'indene' radical (I.4,5). The propionamide group lost C_2H_5CO or C_2H_4CO (I.8 , 10) and the benzamide group lost C_6H_5CO (I.9) followed by fragmentation as for the enamide groups.

2.The mass spectra of the benzoquinoline diones are recorded in appendix I.14.The spectra had a signal corresponding to a M+2 species, indicative of the presence of incompletely oxidised compound , m/z 211.



m/z 211

The dione rearranges and eliminates CO to yield the indenopyridone (8) as the most abundant ion, m/z 181 (100%).Fractionation follows that of (8), eliminating CO followed by elimination of HCN as a neutral species.

3.The diazoketones (appendix I.15 , 18) lost nitrogen and underwent a Wolff rearrangement in the mass spectrometer to give the ketene (100%), m/z 193 and m/z 192 respectively.Subsequent loss of CO gave the parent compound as the most abundant ion (m/z 165 and m/z 166 respectively.)

4.The fractionation routes observed with the esters are detailed in appendix I.16 ,22 and 23. They give the parent heterocycle at m/z 166 via loss of CO followed by loss of OCH_3 or $OCH_2C_6H_5$.
The α-hydroxy ester (appendix I.21) loses CO and OCH_3 to give the 5-hydroxy compound at m/z 182.
The amide (appendix I.19) loses $CONHC(CH_3)_3$ to give the parent heterocycle at m/z 166 (100%).

5.The parent indenopyridine, 5H-indeno[1,2-b]pyridine (4) eliminates HCN as a neutral species to give a [6,5,4] tricyclic fragment. In the case of the oxo compound (8) the fragmentation proceeds by loss of CO. (appendix I. 31 and 27 respectively).

6.5-Hydroxy-5H-indeno[1,2-b]pyridine (208),appendix I.28, loses H$^\bullet$ to give the planar hydroxy and oxo species,loss of CO gives the [6,4,6] fragment followed by loss of HCN to give the [6,4,4] fragment. Alternatively loss of OH$^\bullet$ gave the parent species at m/z 166.

7.The mass spectra of 9,9'-bifluorenyl (217) had a molecular ion at m/z 330 which underwent facile cleavage at the 5 position to give the parent species m/z 165 (100%).

8.The fragmentation routes observed for the alcohols are detailed in appendix I.32,33,33i,34,35 .Loss of $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, $(CH_2)_3CH_3$, C_6H_5 and C_6H_5 respectively led to a planar hydroxy species, loss of CO gave the [6,4,6] fragment.

9. In general, the oximes loose an O$^{\bullet\bullet}$ diradical, followed by loss of HCN, or alternatively the oxime rearranges to N=O which is then eliminated (NO$^{\bullet}$) to give the parent species, as indicated by their mass spectra (appendix I.36, I.39).For the bromo- derivative (appendix I.55),loss of the bromo radical proceeds loss of the O$^{\bullet\bullet}$ diradical. For the NO_2 derivative (appendix I.56),loss of NO_2occurs first,followed by the oxygen diradical.Alternatively, the nitro- group may rearrange to N=O which is then eliminated to give the parent species.

10.The mass spectra of the bromo- derivatives are given in appendices I.42,43,44,45 and 46.In each case the presence of the Br group is confirmed by the bromo ratio seen at the molecular ion.For example, for a monobromo compound the ratio is $M^{+\bullet}$: M + 2 seen as a 1:1 ratio.For a dibromo compound this ratio is 1:2:1, and a tribromo compound 1:2:2:1. In each case loss of a Br radical gives the parent species (m/z 166),appendix I.44.For the pyridone derivatives,this is followed by loss of CO.Alternatively loss of CO may proceed loss of the bromine radical. (appendix I.42,43). The other bromo compounds follow a similar route, ie loss of bromine radicals to give the parent indenopyridine (m/z 166).

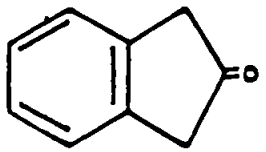
11.Mass spectra of the nitro derivatives indicate three pathways by which fragmentation may occur.Direct loss of NO_2 gives the parent indenopyridine, or loss of an oxygen diradical, followed by loss of NO also gives the parent indenopyridine.For the indenopyridone, the third route of fragmentation idicates loss of CO.(appendix I.47,48).

The amines (appendix I.49,50) loose a H• followed by HCN to give a [5,4,6] fragment.
The alcohols (appendix I.51,52) loose OH• to give the parent heterocycle.Normal fragmentation then occurs.

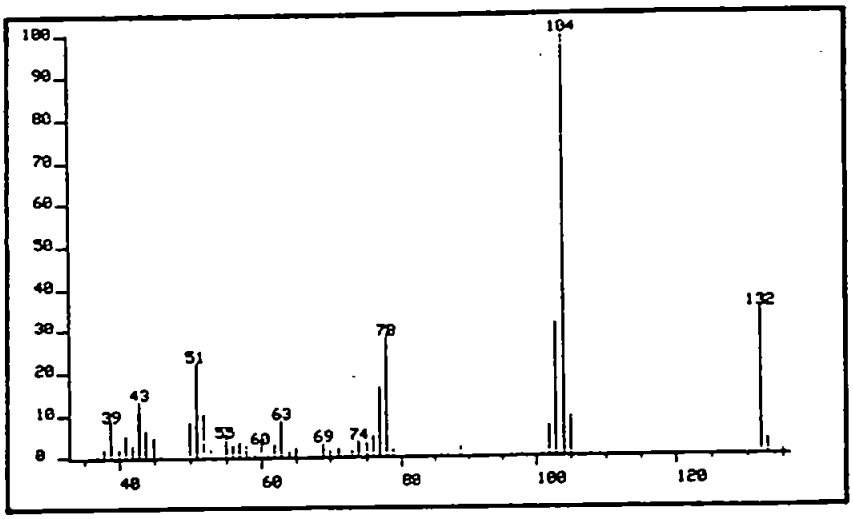
12.The 5-acetamido derivative (230), appendix I.53 may loose $COCH_3$ to give a planar amine (m/z 181),or may loose CH_2=C=O to give the amine (m/z 182).Alternatively, loss of $NHCOCH_3$ gives the parent indenopyridine.
The mass spectra of the diacetamido derivative (246), is very similar.Loss of $COCH_3$,followed by loss of $NHCOCH_3$ gives the diamine (m/z 196).Alternatively loss of $NHCOCH_3$ and CH_2=C=O gives the amine (m/z 181).
For the 5-acetamido,7-nitro- derivative,loss of NO_2 proceeds loss of $NHCOCH_3$ which leads to the parent indenopyridine (m/z 166).

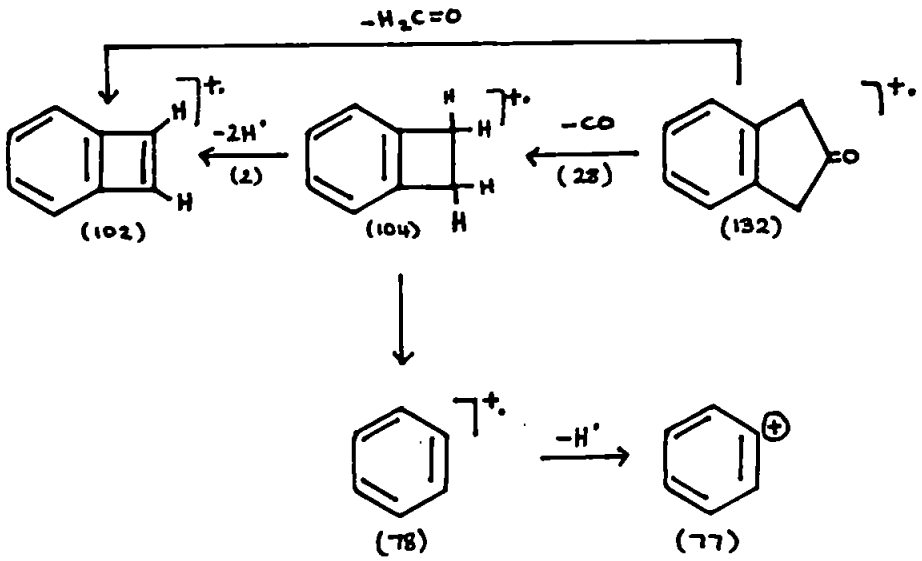
13.The mass spectra of the N-oxides (appendix I,60,61,62 and 63) are characterised by the loss of an oxygen di-radical (O••) which leads to the parent heterocycle.
For the nitro compounds,loss of the O•• is followed by normal loss of the NO_2 group (as discussed in 11.)

Appendix 1.1 2-Indanone (168)

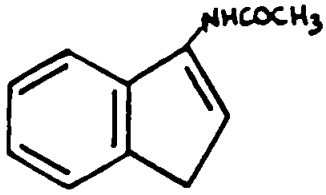


C_9H_8O RMM=132

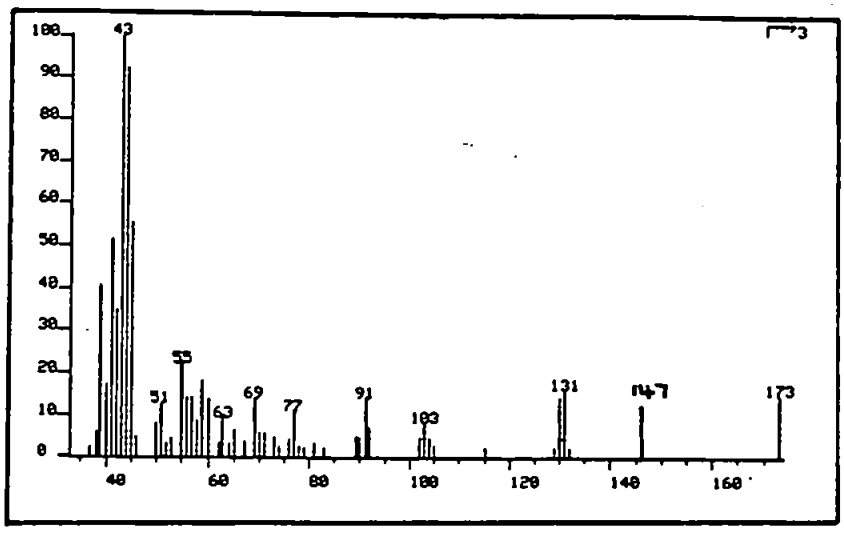




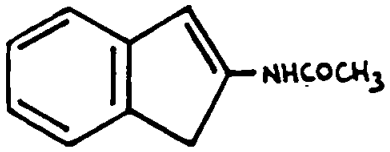
Appendix 1.2 Attempted preparation of 1-acetamido-indene (182)



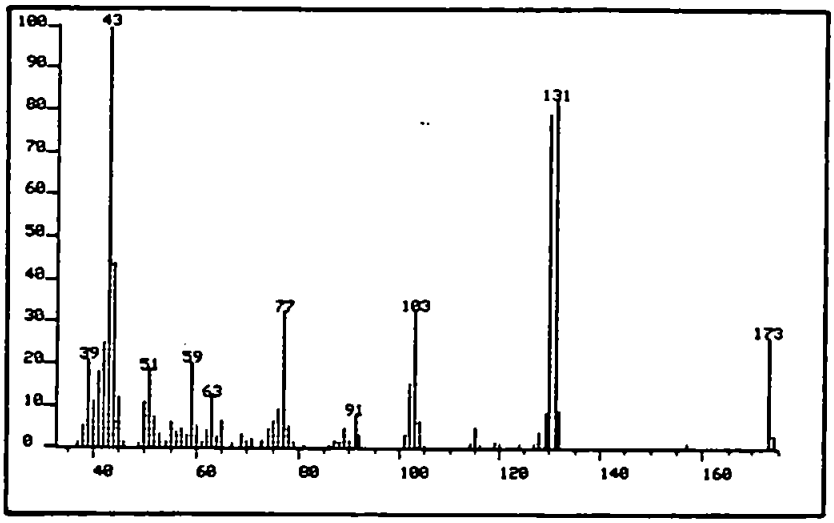
$C_{11}H_{11}NO$ RMM=173

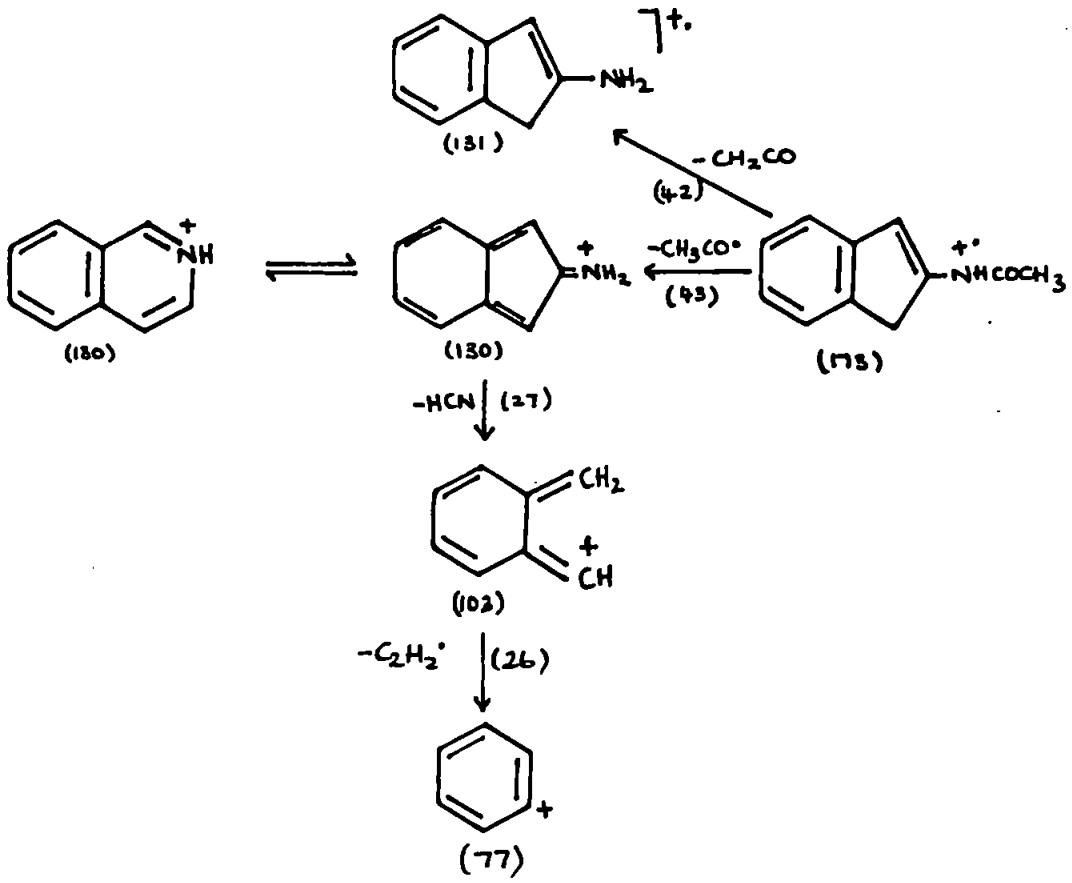


Appendix 1.3 2-acetamidoindene (183)

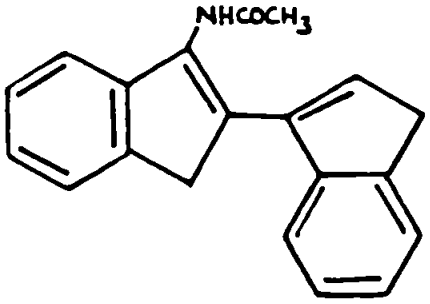


$C_{11}H_{11}NO$ RMM=173

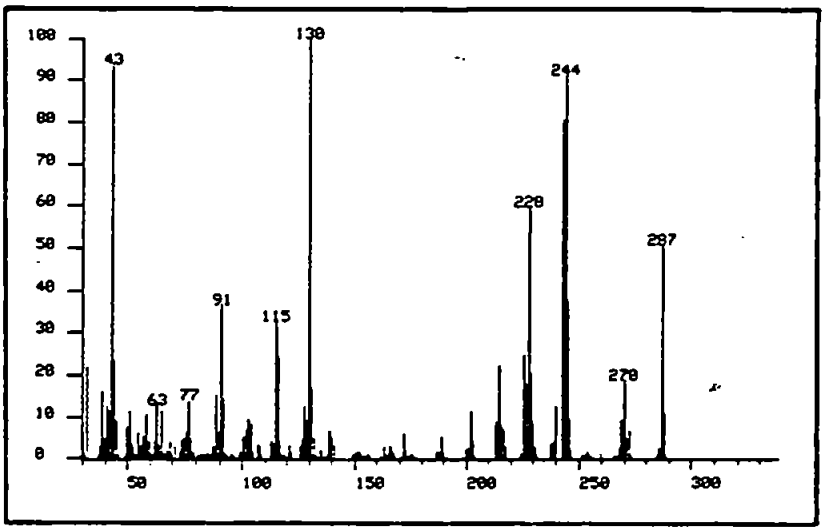


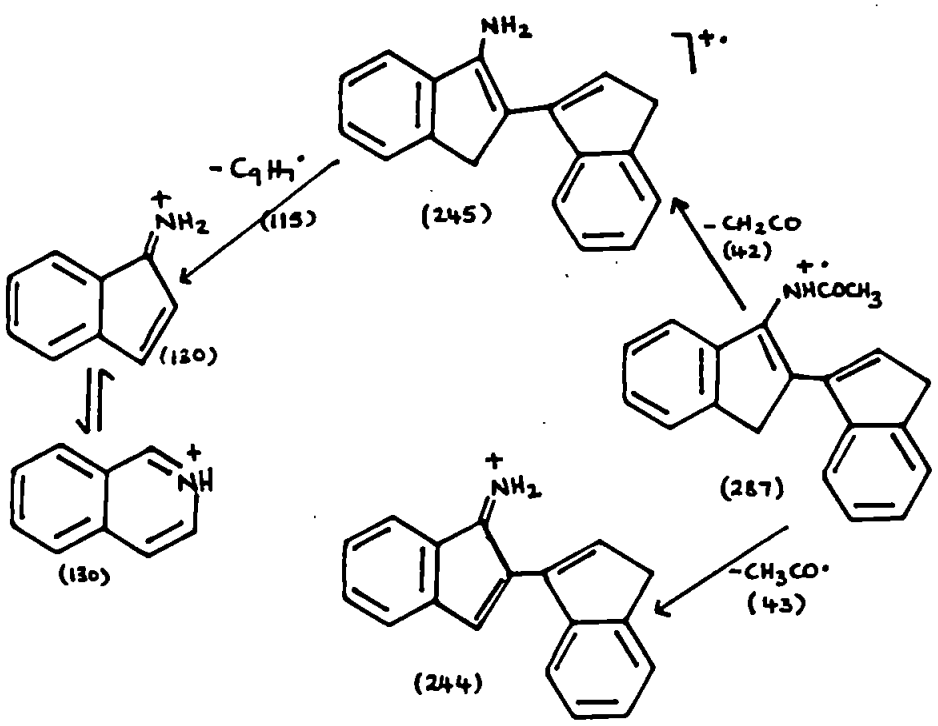


Appendix 1.4 1-acetamido-2(1'-indenyl)indene (184)

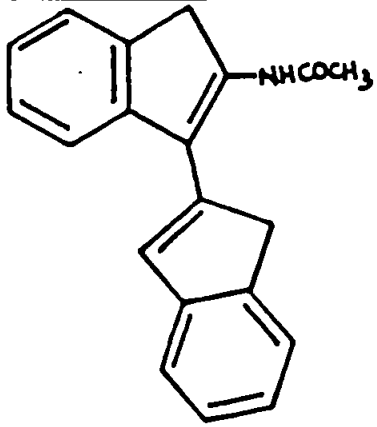


$C_{20}H_{17}NO$ RMM=287

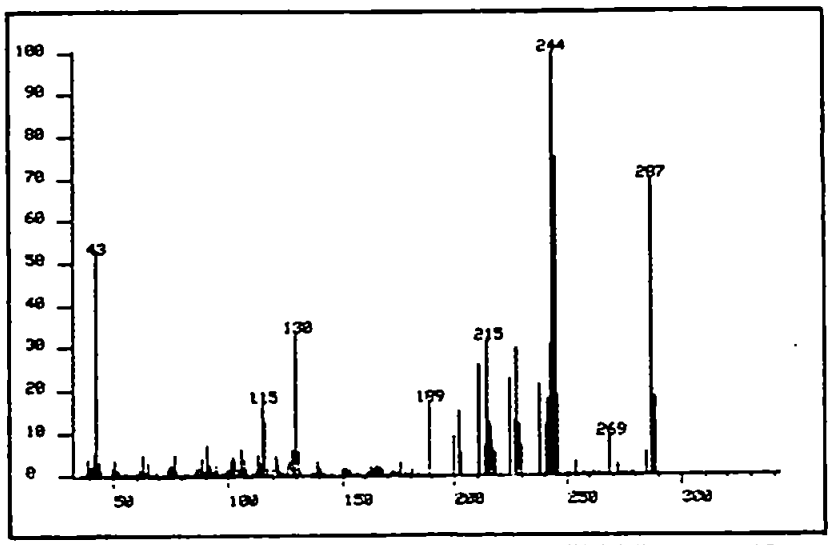


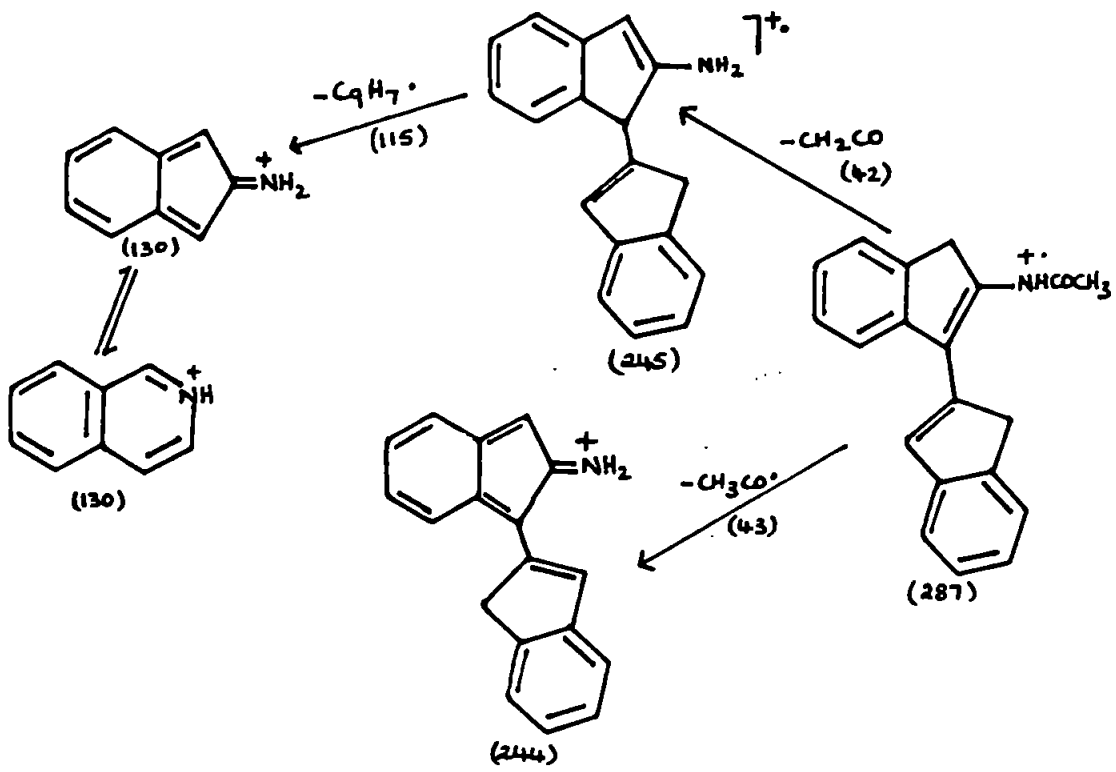


Appendix 1.5 2-acetamido-1(2'-indenyl)indene (185)

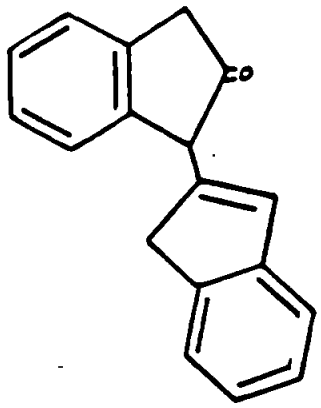


$C_{20}H_{17}NO$ RMM=287

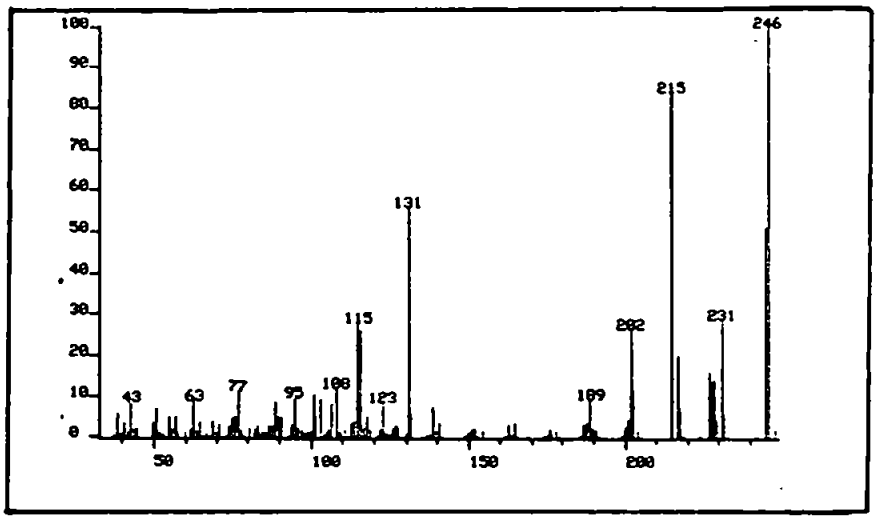


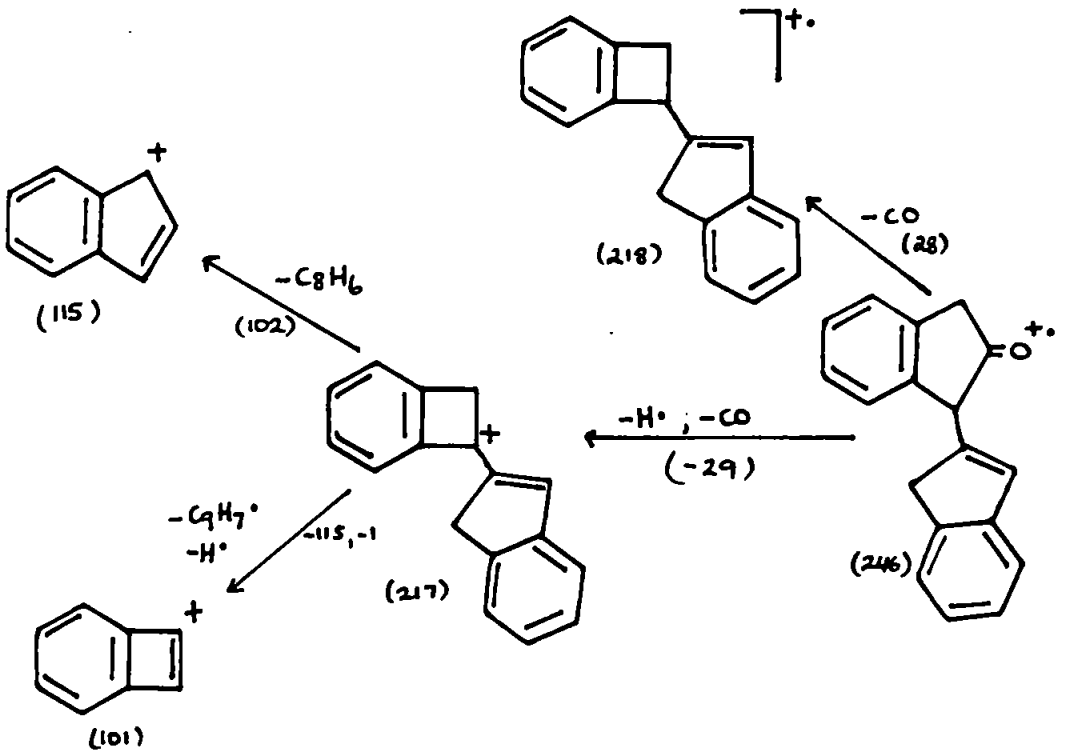


Appendix 1.6 1(2'-indanylidenyl)indan-2-one (188)

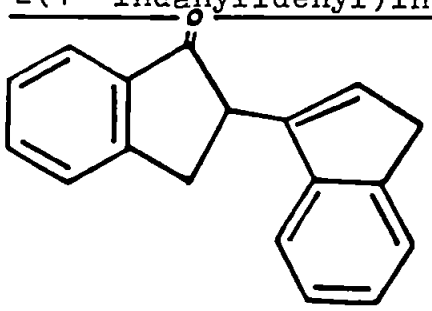


$C_{18}H_{14}O$ RMM=246

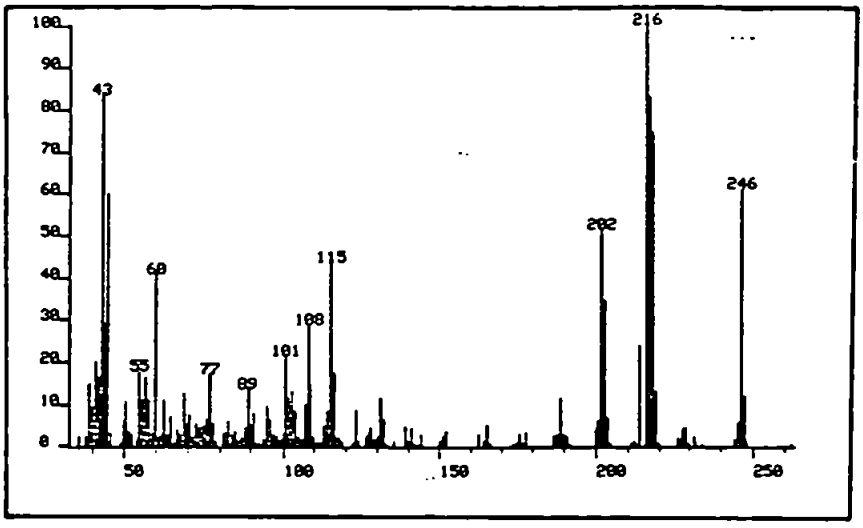


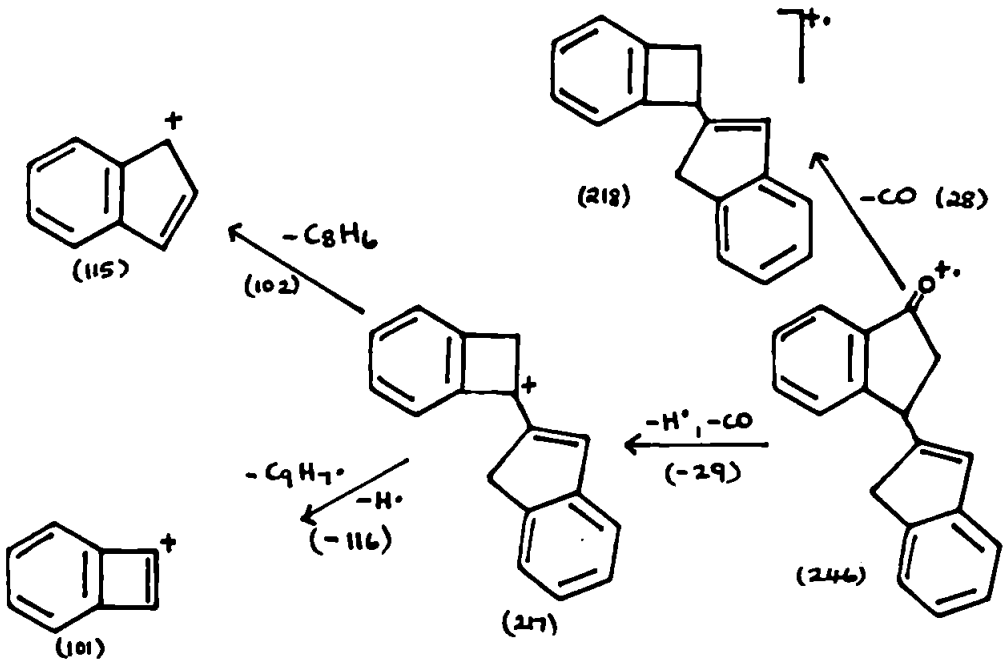


Appendix 1. 7 2(1'-indanylidenyl)indan-1-one (189)

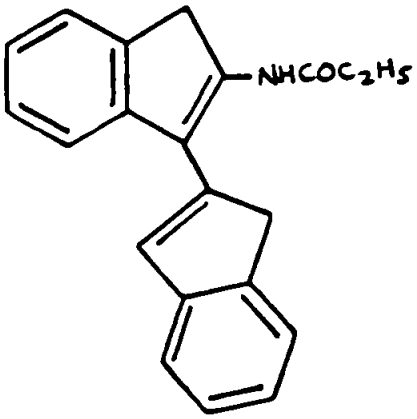


$C_{18}H_{14}O$ RMM=246

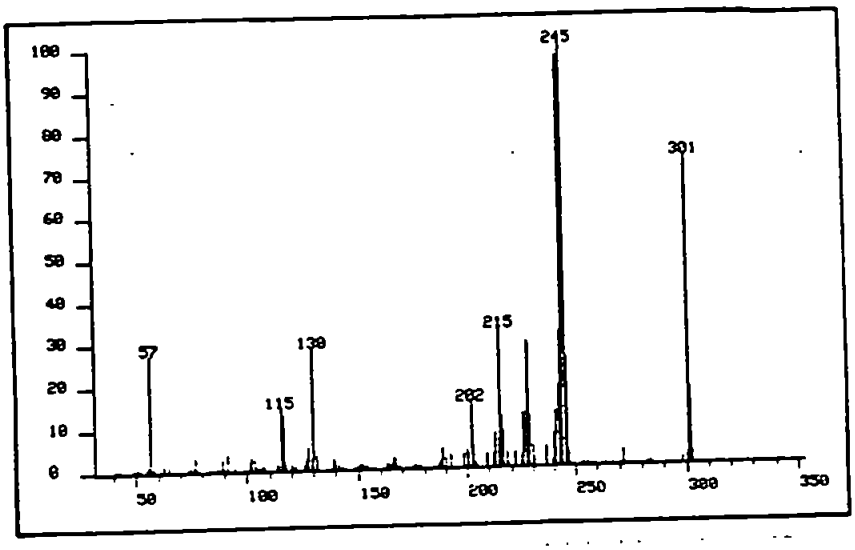


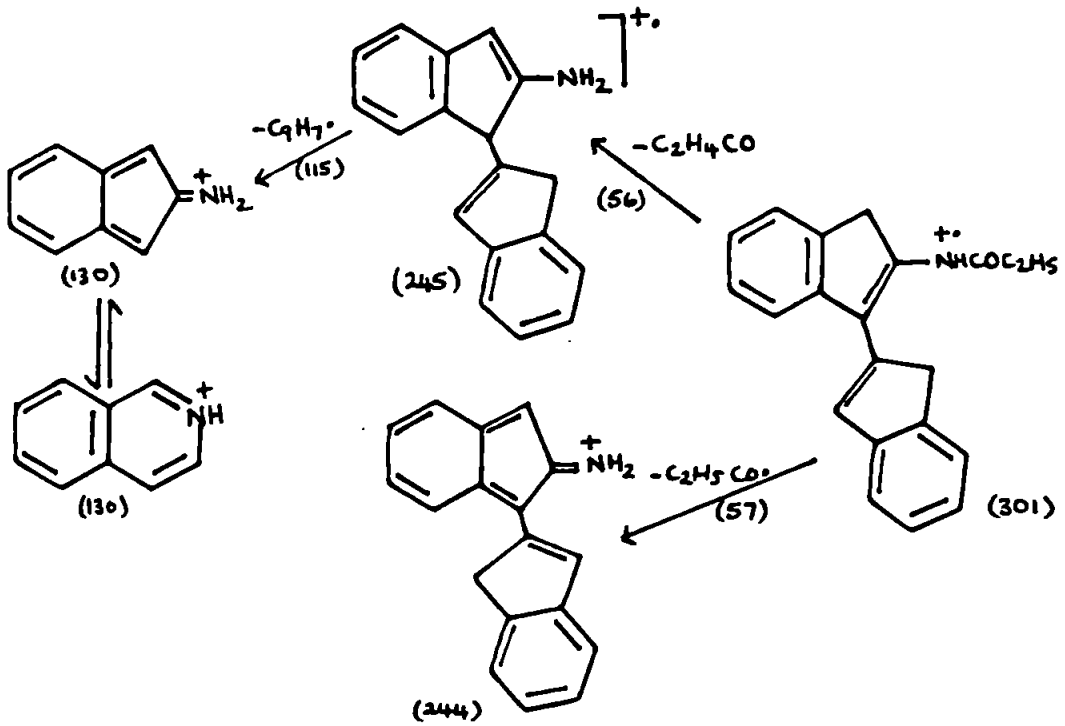


Appendix 1.8 2-propionamido-1(2'-indenyl)indene (190)

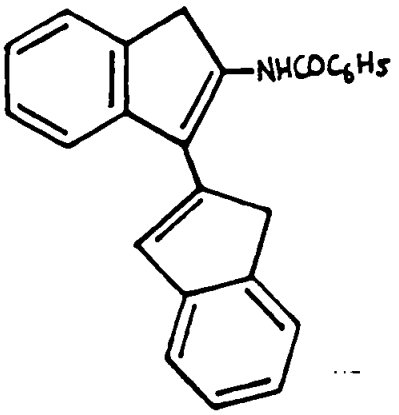


$C_{21}H_{19}NO$ RMM=301

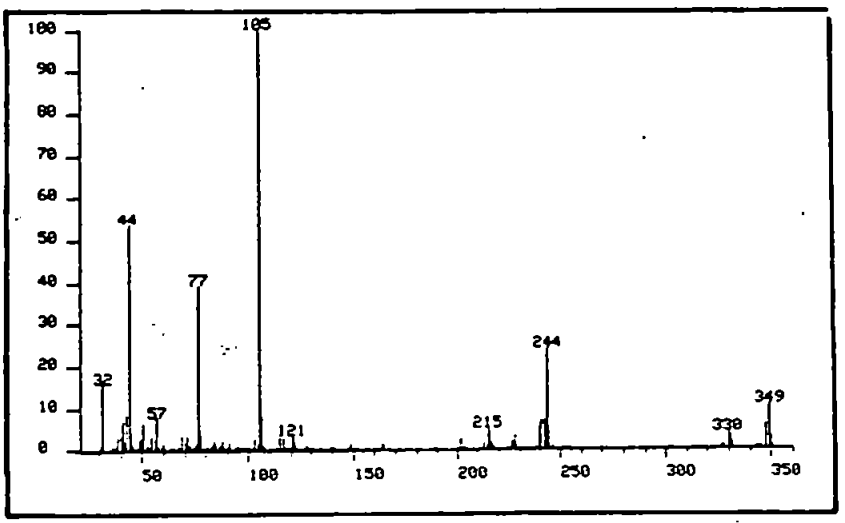


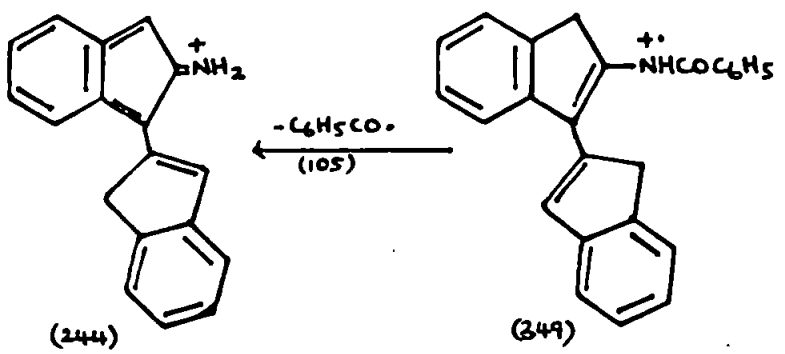


Appendix 1.9 2-benzamido-1(2'-indenyl)indene (191)

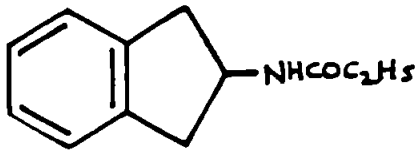


$C_{25}H_{19}NO$ RMM=349

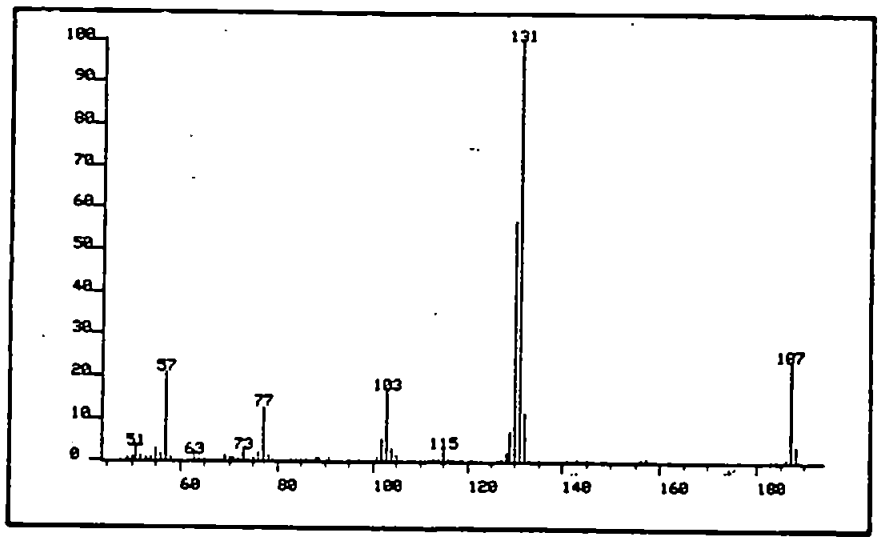


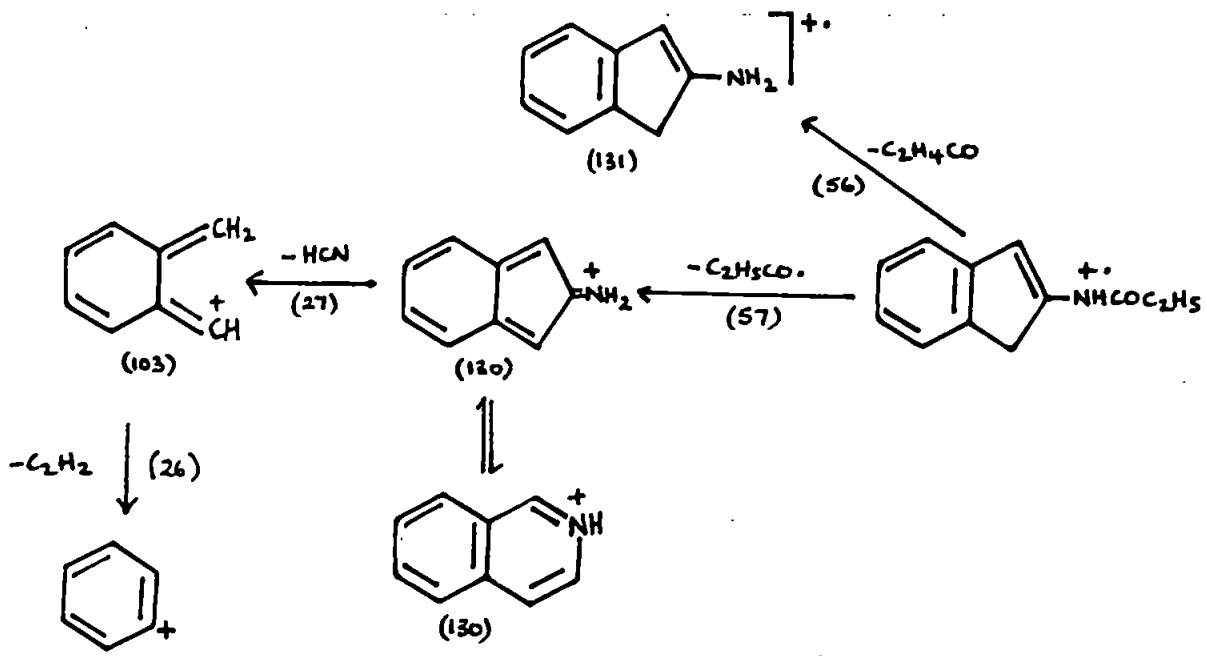


Appendix 1.10 2-propionamidoindene (192)

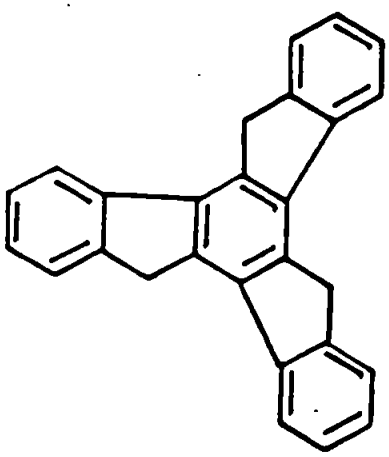


$C_{12}H_{13}NO$ RMM=187

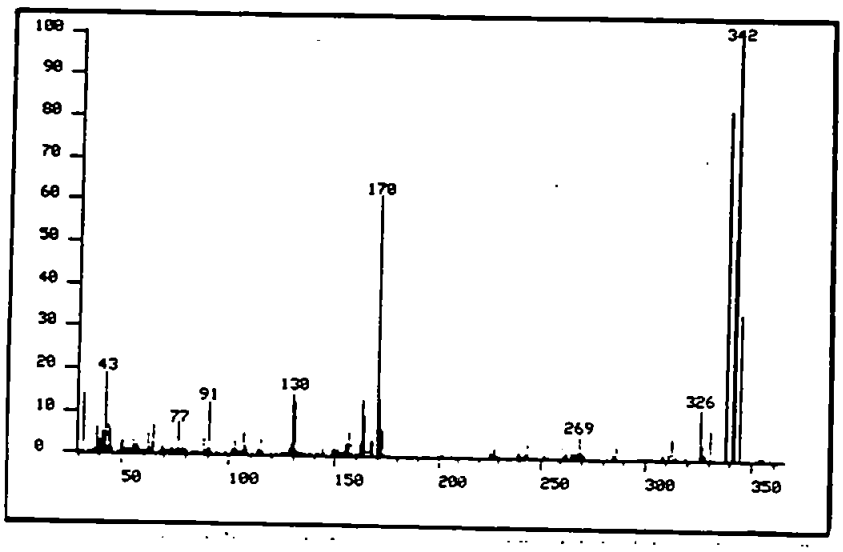




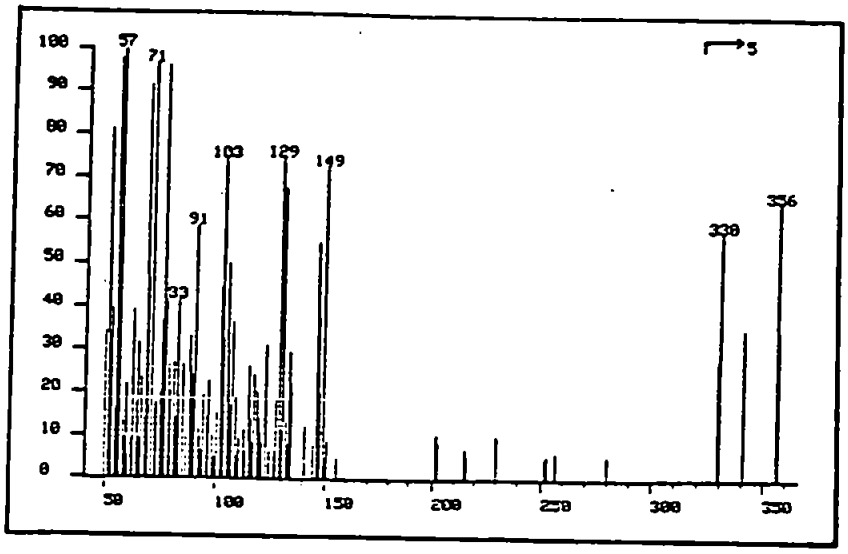
Appendix 1.11 10,15-Dihydro-5H-indeno[1,2-a;1',2'-c]-fluorene , 'Truxene'. (193)



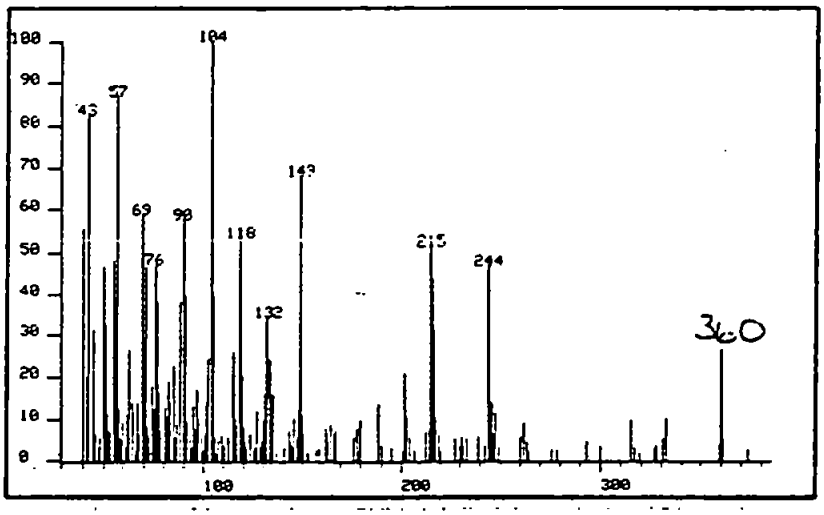
$C_{27}H_{18}$ RMM=342



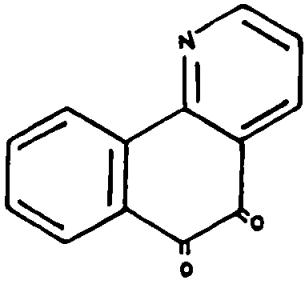
Appendix 1.12 Spectra of solid with RMM 356.



Appendix 1.13 Spectra of solid with RMM 360.

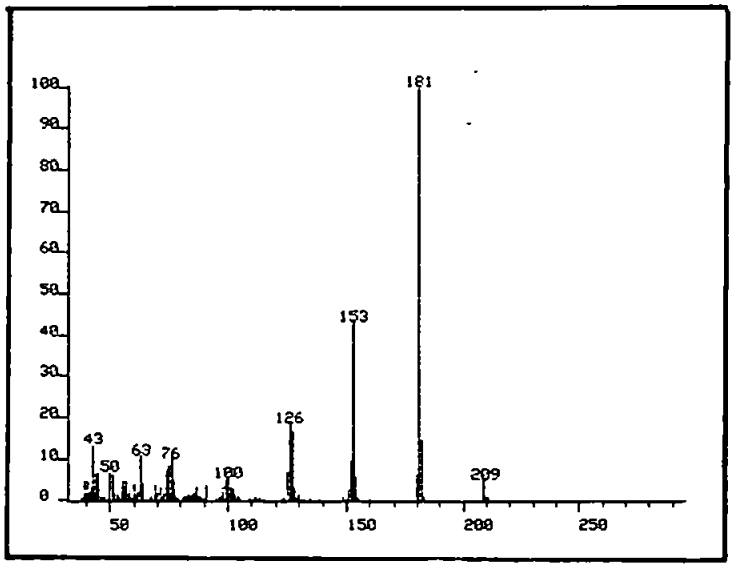


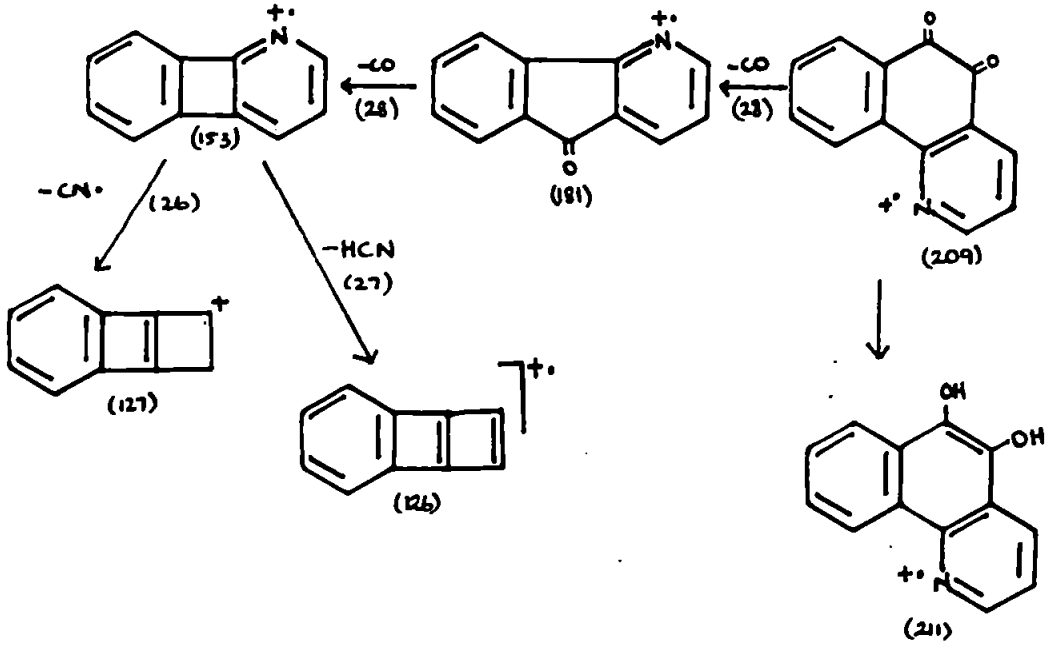
Appendix 1.14 Benz[h]quinolin-5,6-dione (99)



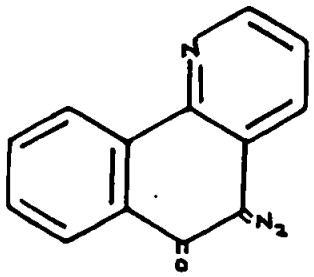
$C_{13}H_7NO_2$

RMM=209

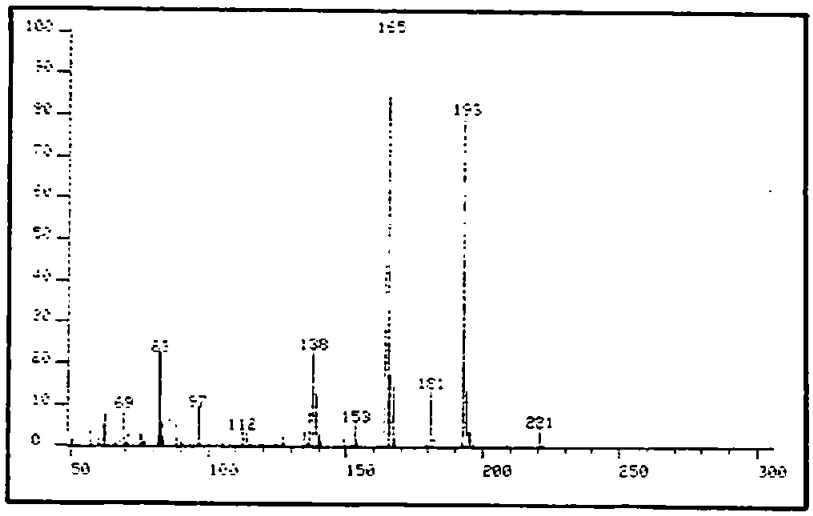


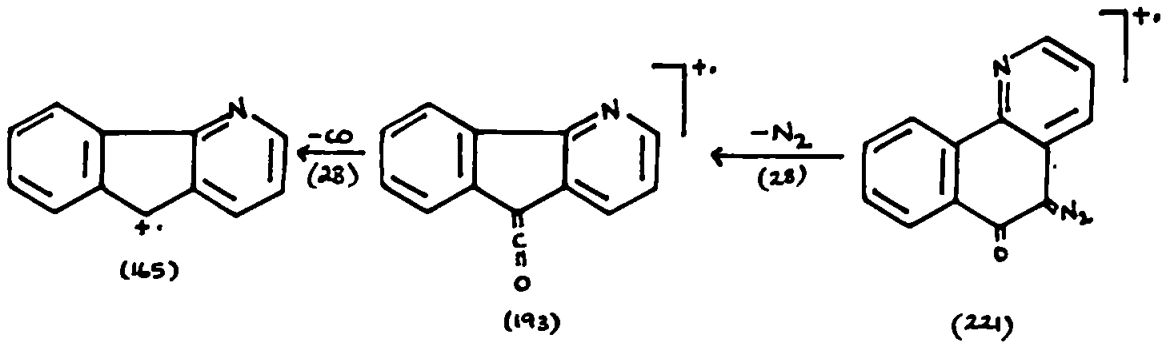


Appendix 1.15 Benz[h]quinolin-5,6-diazoketone (186)

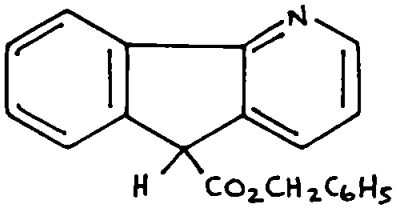


$C_{13}H_7N_3O$ RMM=221

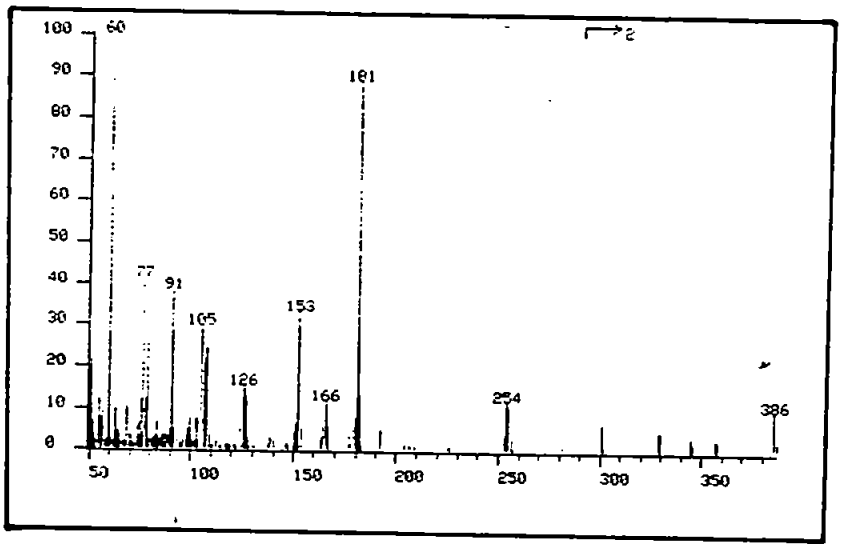




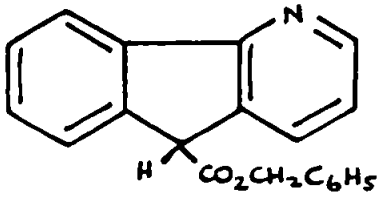
Appendix 1.16 Fraction III showing evidence of benzyl-5H-indeno [1,2-b] pyridine-5-carboxylate (207)



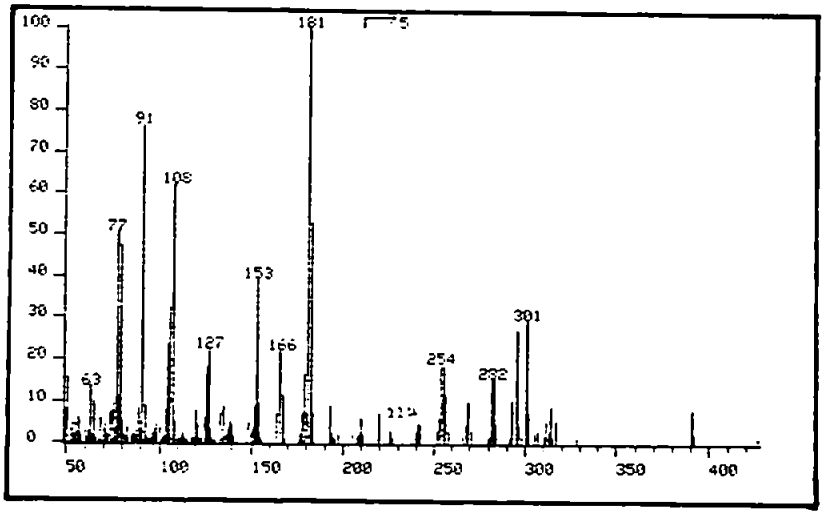
$C_{20}H_{15}NO_2$ RMM=301

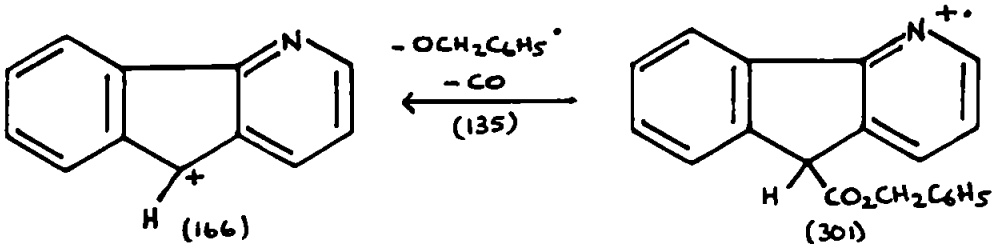


Appendix 1.17 Fraction IV showing evidence of benzyl-5H-indeno[1,2-b]pyridine-5-carboxylate (207)

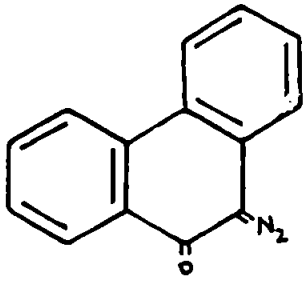


$C_{20}H_{15}NO_2$ RMM=301

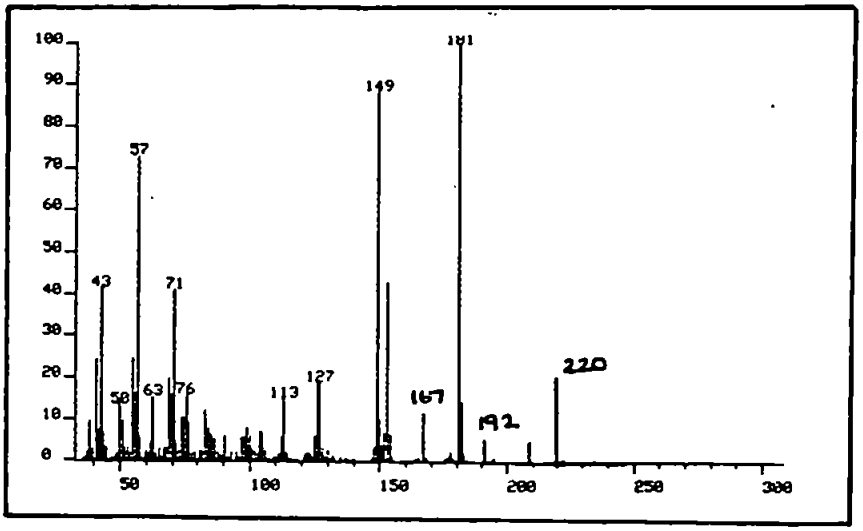


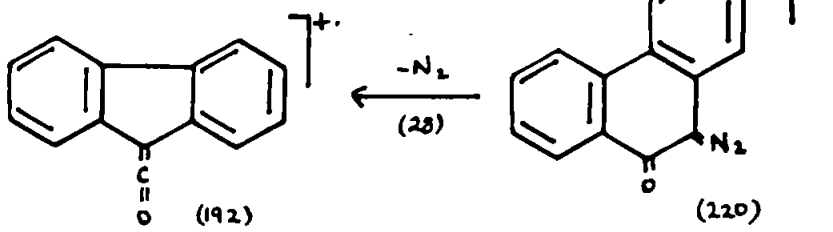


Appendix 1.18 9-diazo-10-phenanthrone (195)

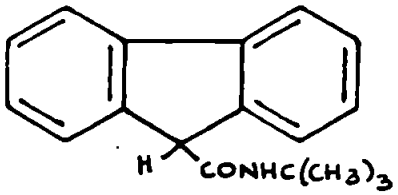


$C_{14}H_8N_2O$ RMM=220

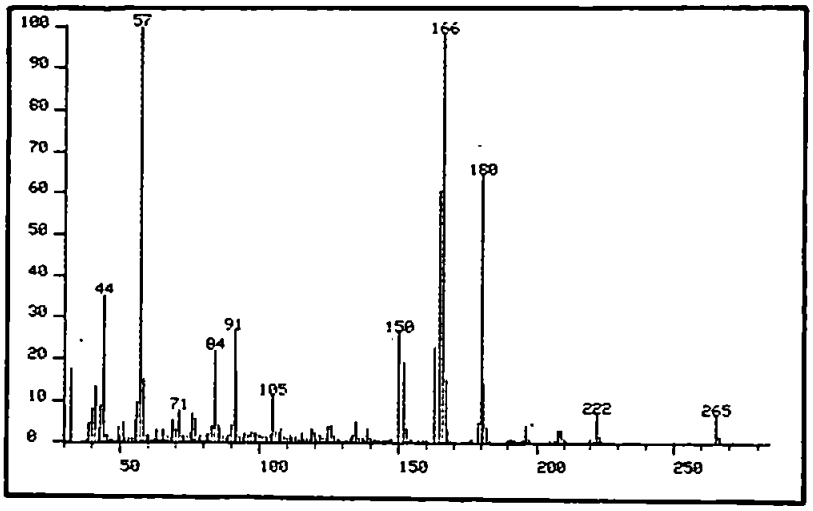


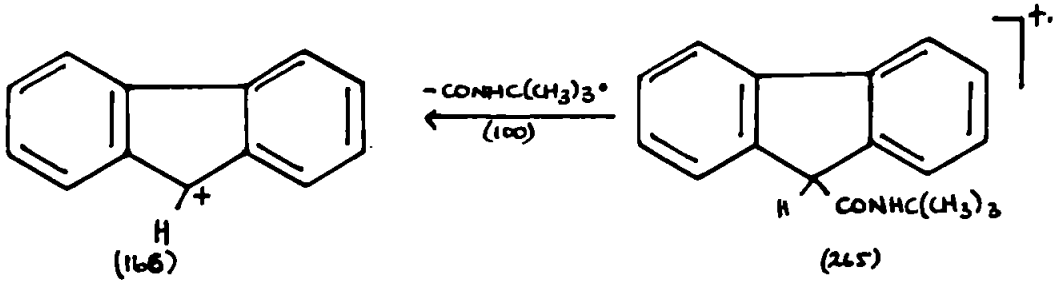


Appendix 1. 19 9H-fluorene-9-tertbutylcarboxemide (197)

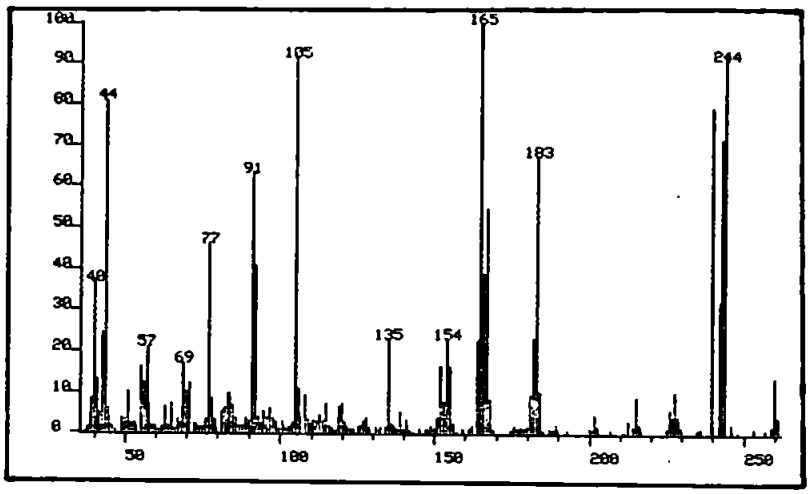


$C_{18}H_{19}NO$ RMM=265

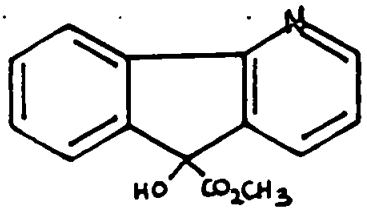




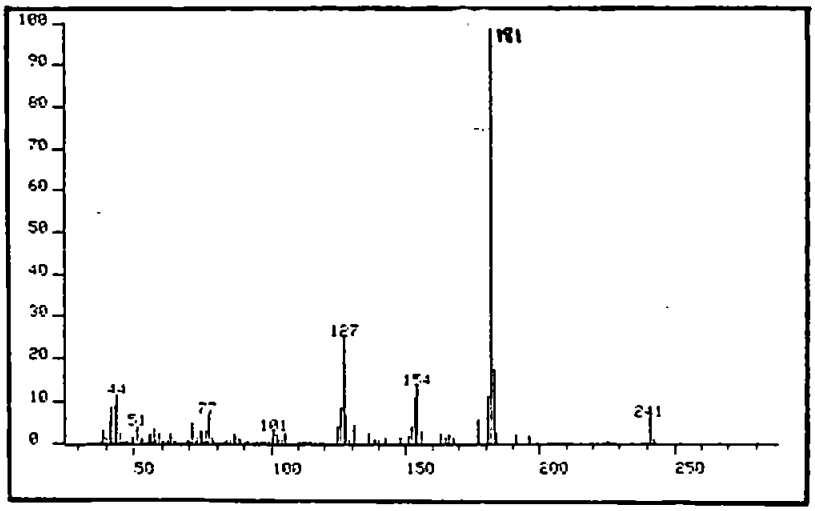
Appendix 1.20 Component (Rf 0.46) showing evidence of indenopyridine fragments.

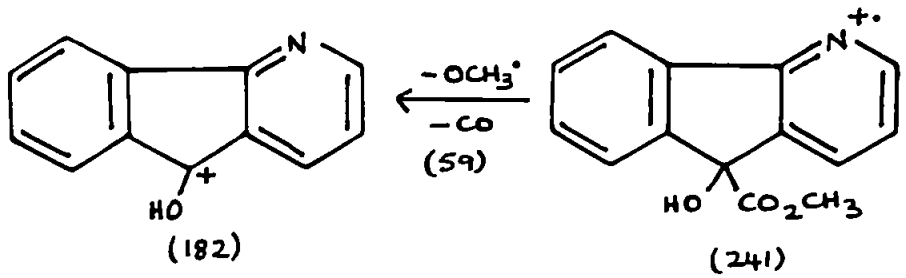


Appendix 1.21 Component (Rf 0.55) showing evidence of (RS)Methyl-5-hydroxyindeno[1,2-b]pyridine-5-carboxylate (198)

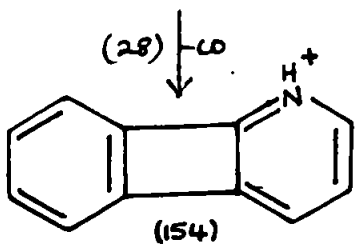


$C_{14}H_{11}NO_3$ RMM=241

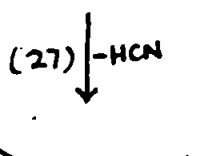


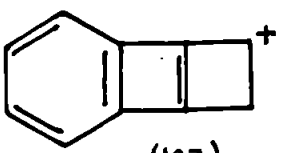


(182) (241)



(154)

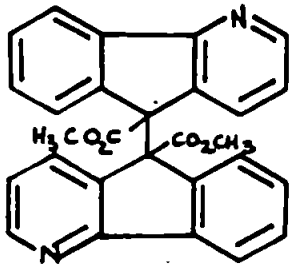




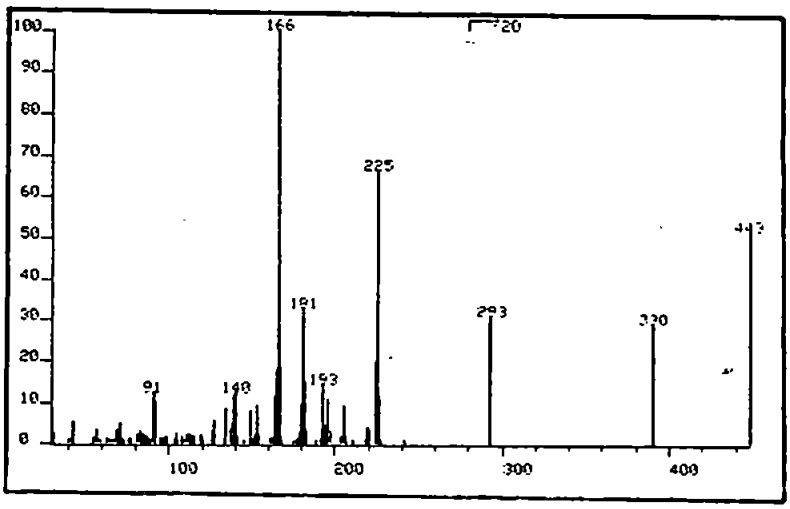
(127)

Appendix 1.22

Component (Rf 0.42) showing evidence of bis-5,5'(methyl-5H-indeno[1,2-b]pyridine-5-carboxylate (194)

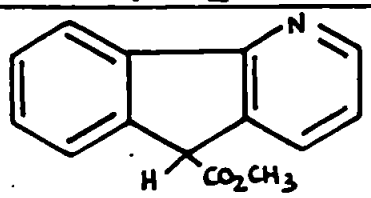


$C_{28}H_{20}N_2O_4$ RMM=448

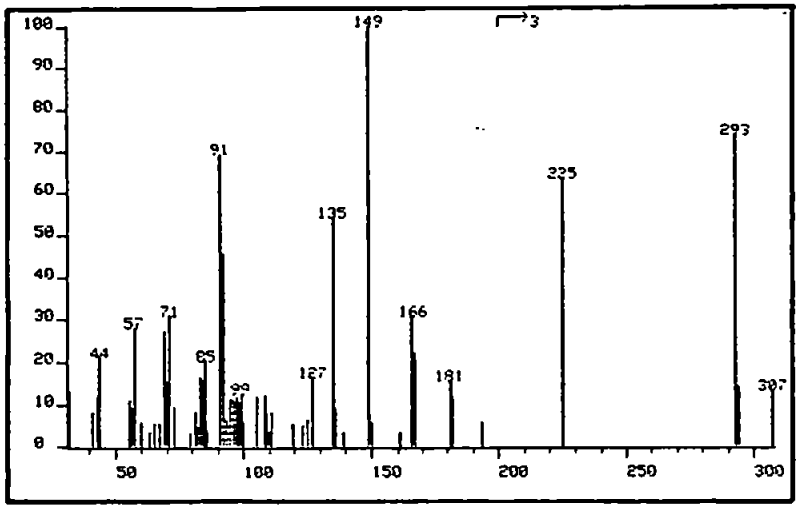


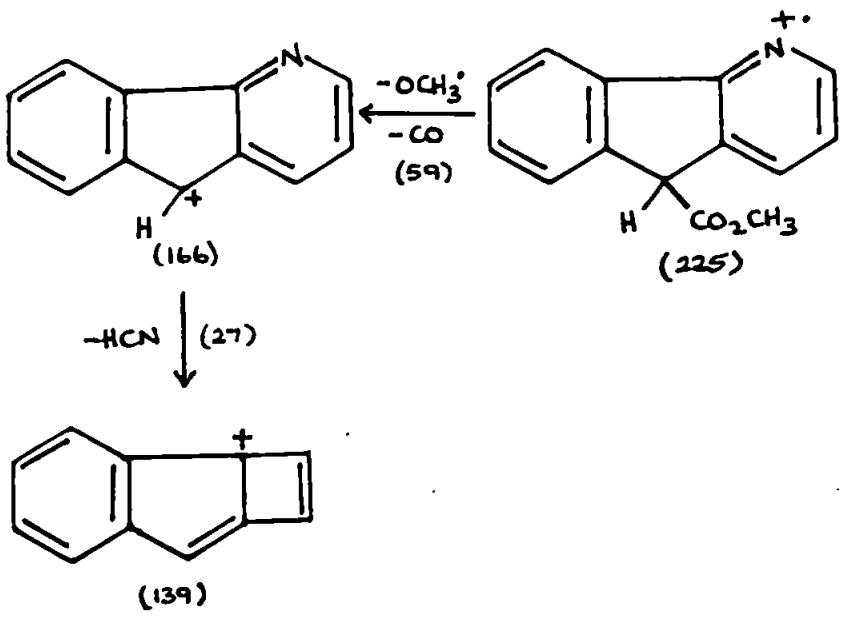
Appendix 1.23

Component (Rf 0.26) showing evidence of (RS)Methyl-5H-indeno[1,2-b]pyridine-5-carboxylate (187)

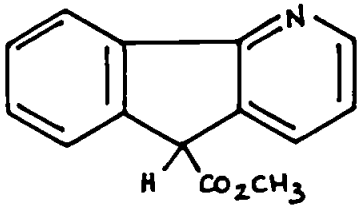


$C_{14}H_{11}NO_2$ RMM=225

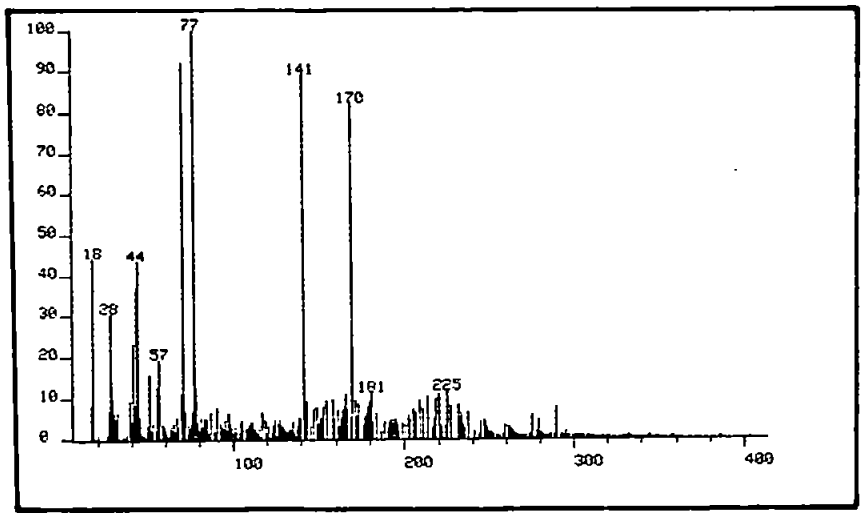




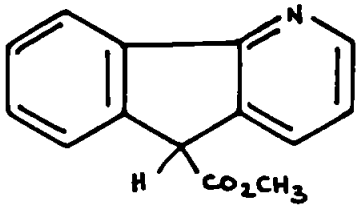
Appendix 1.24 Component (Rf 0.57) showing evidence of (187)



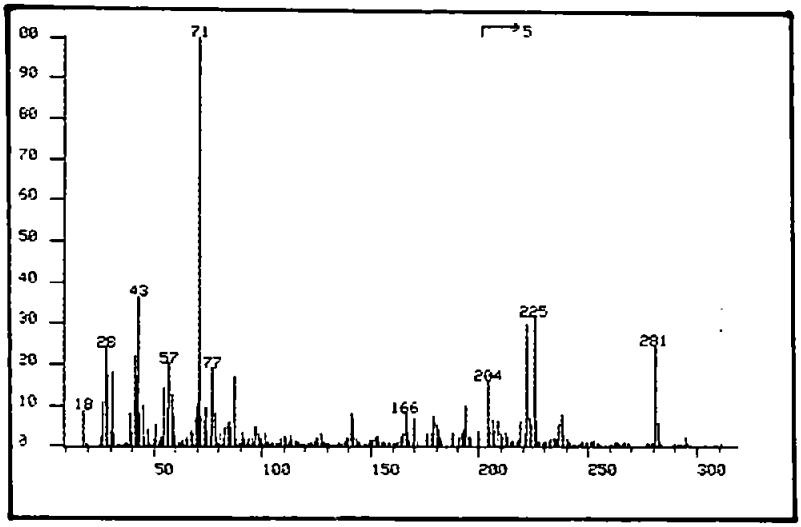
$C_{14}H_{11}NO_2$ RMM=225

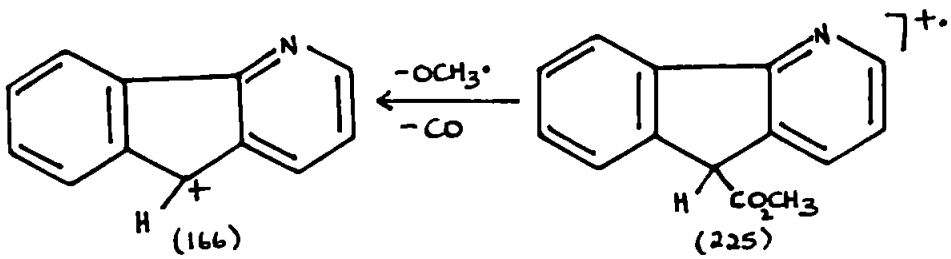


Appendix 1.25 Component (Rf 0.77) showing evidence of (187).

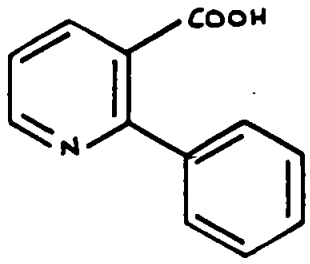


$C_{14}H_{11}NO_2$ RMM=225

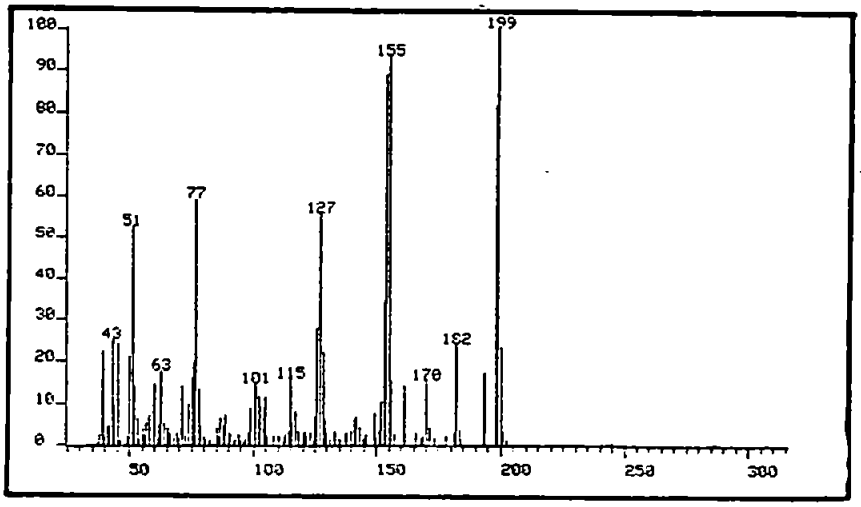


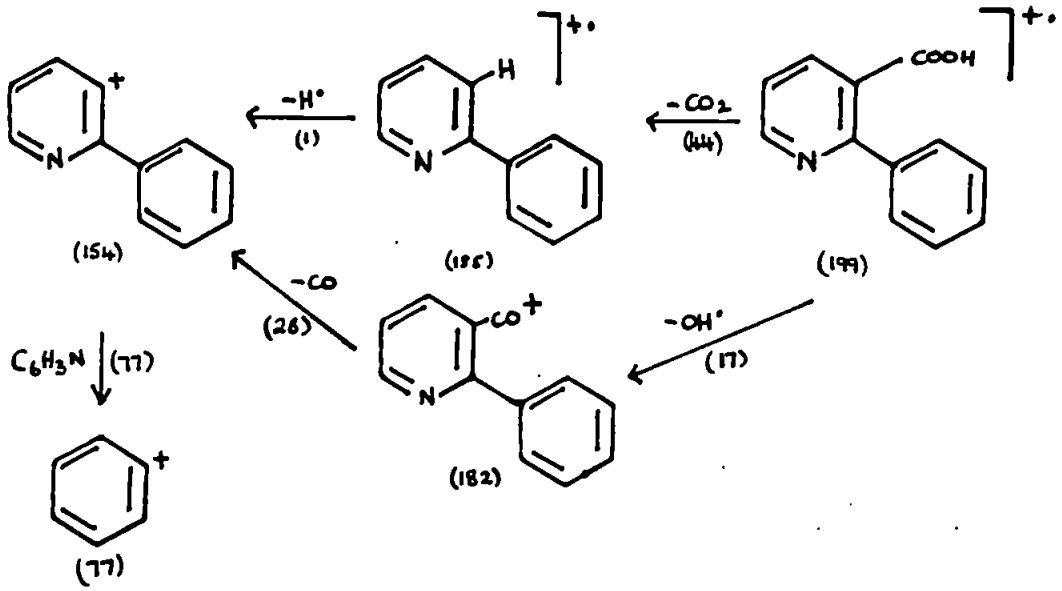


Appendix 1.26 2-phenyl-3-pyridine carboxylic acid (158)

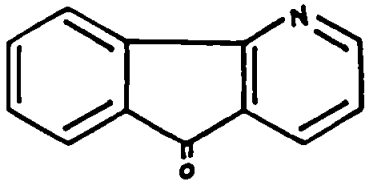


$C_{12}H_9NO_2$ RMM=199

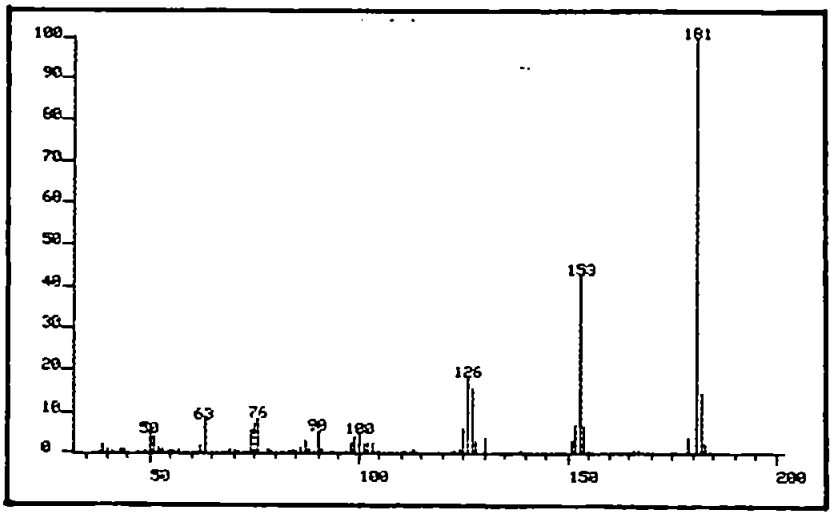


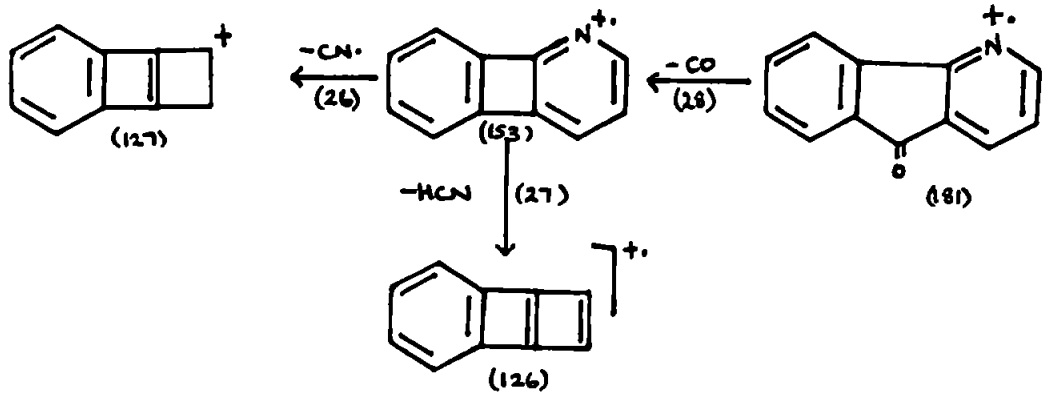


Appendix 1, 27 5H-indeno [1,2-b] pyridin-5-one (8)

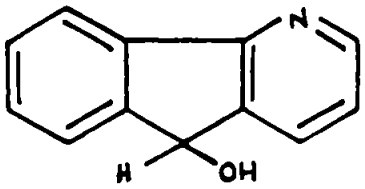


$C_{12}H_7NO$ RMM=181

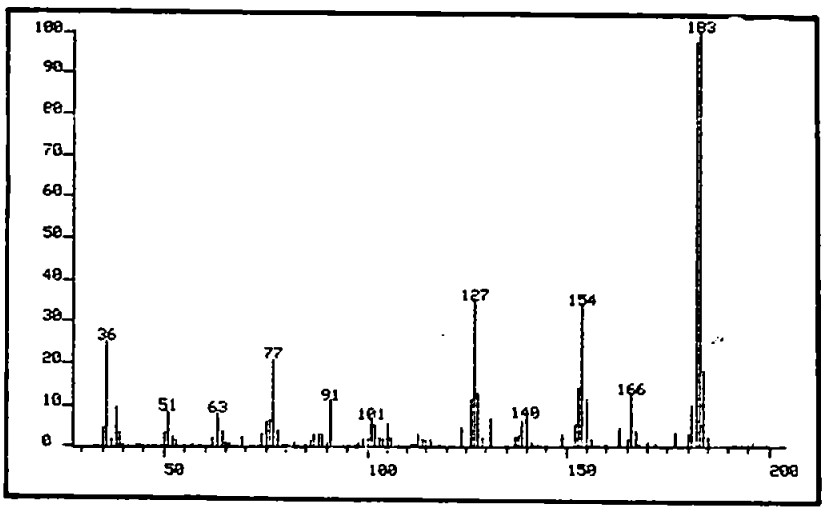


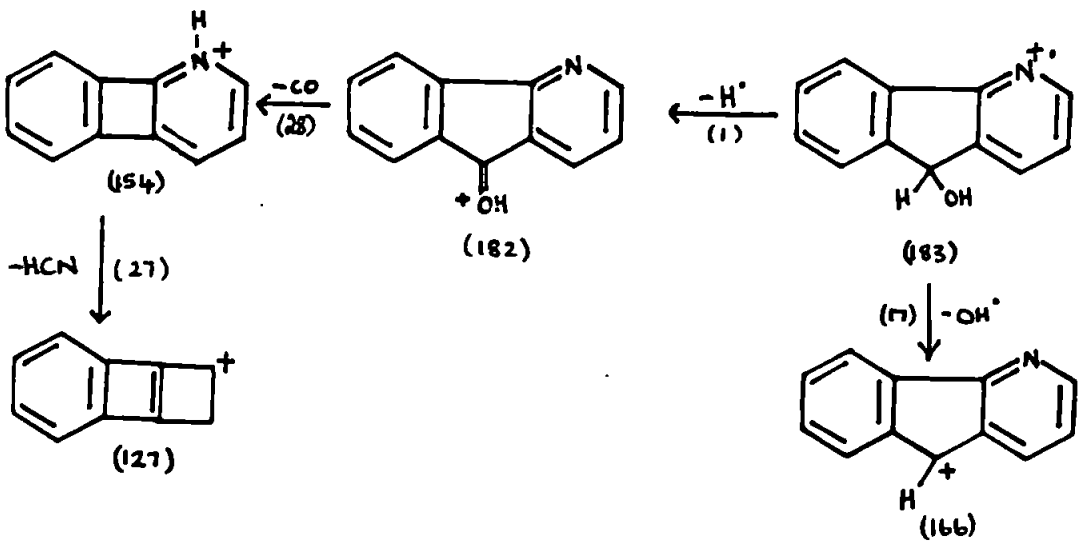


Appendix 1.28 (±)5-hydroxy,5H-indeno [1,2-b] pyridine (208)

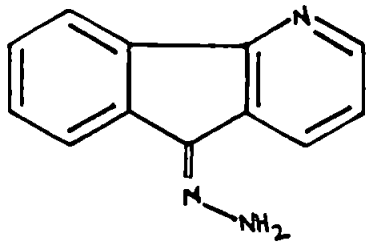


$C_{12}H_9NO$ RMM=183

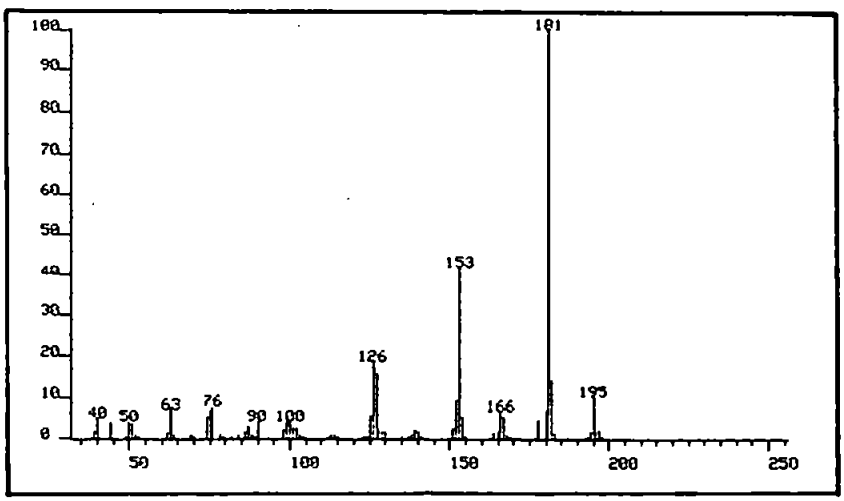


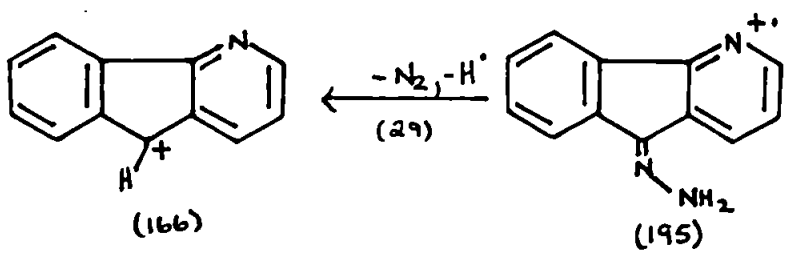


Appendix 1.29 5H-indeno[1,2-b]pyridine-5-one hydrazone (55)

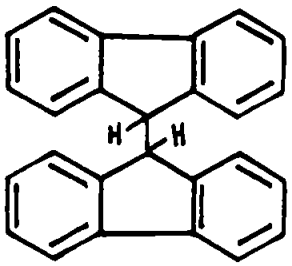


$C_{12}H_9N_3$ RMM=195

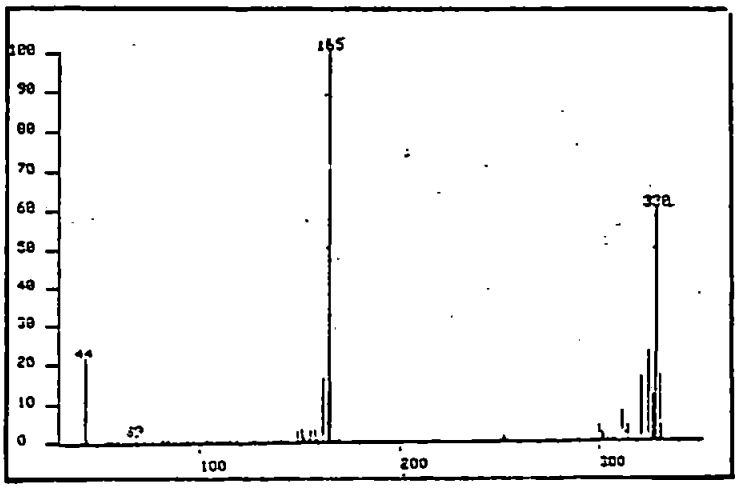


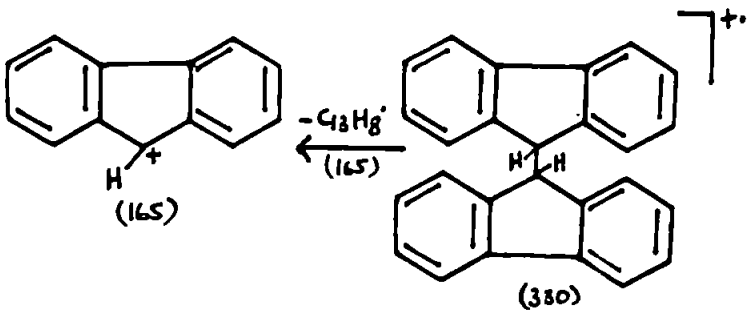


Appendix 1.30 9,9'-bifluorenyl (217)

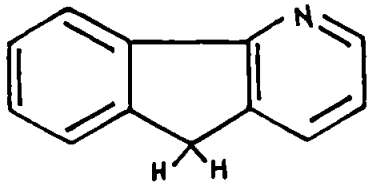


$C_{26}H_{18}$ RMM=330

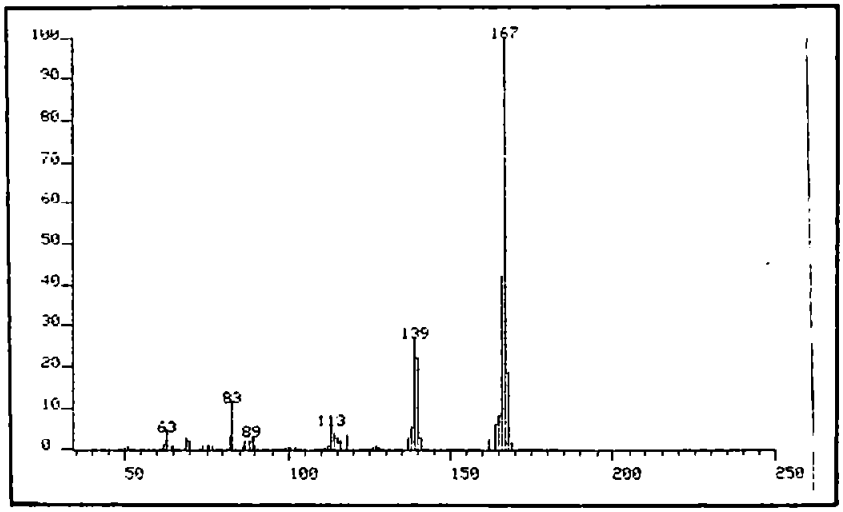


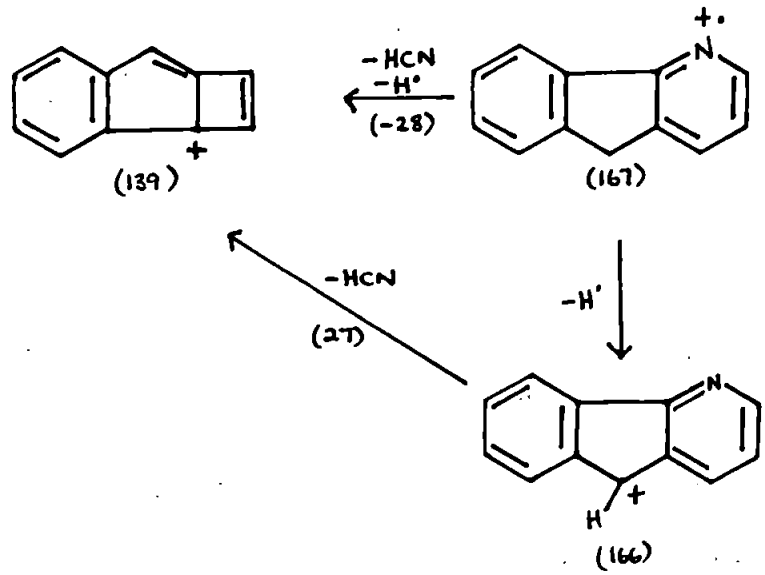


Appendix 1,31 5H-indeno[1,2-b]pyridine (4)

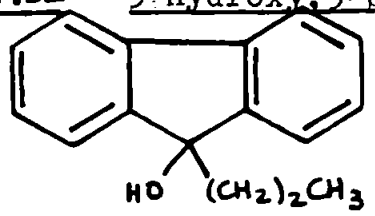


$C_{12}H_9N$ RMM=167

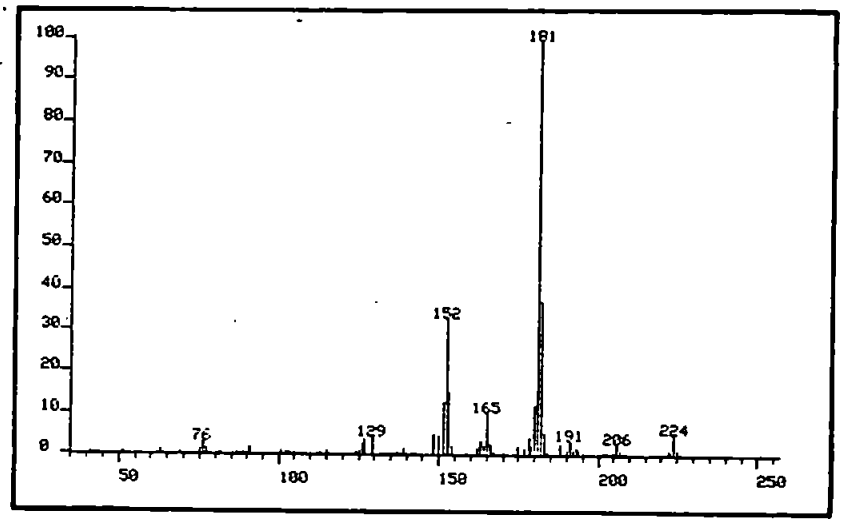


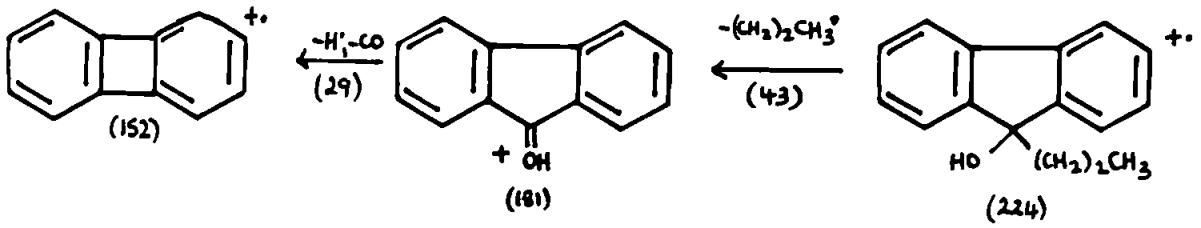


Appendix 1.32 9-hydroxy,9-propylfluorene (218)

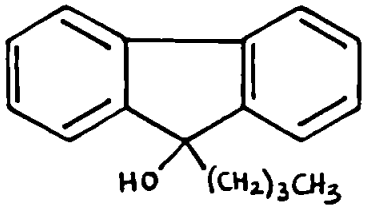


$C_{16}H_{16}O$ RMM=224

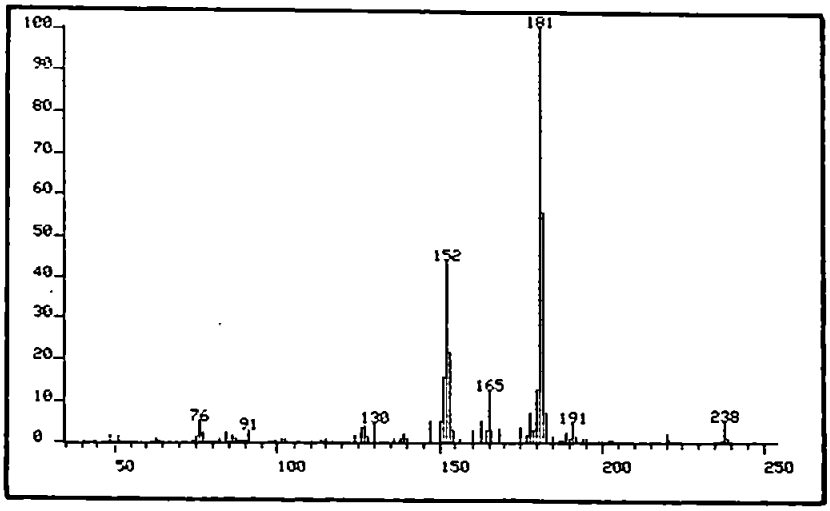


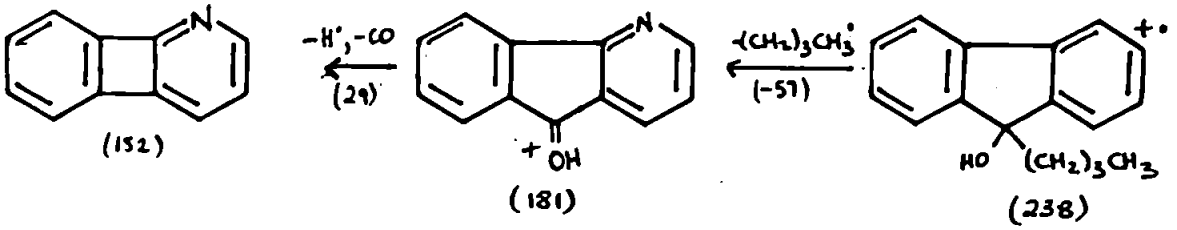


Appendix 1.33 9-butyl-9-hydroxyfluorene (219)

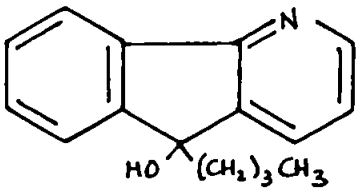


$C_{17}H_{18}O$ RMM=238

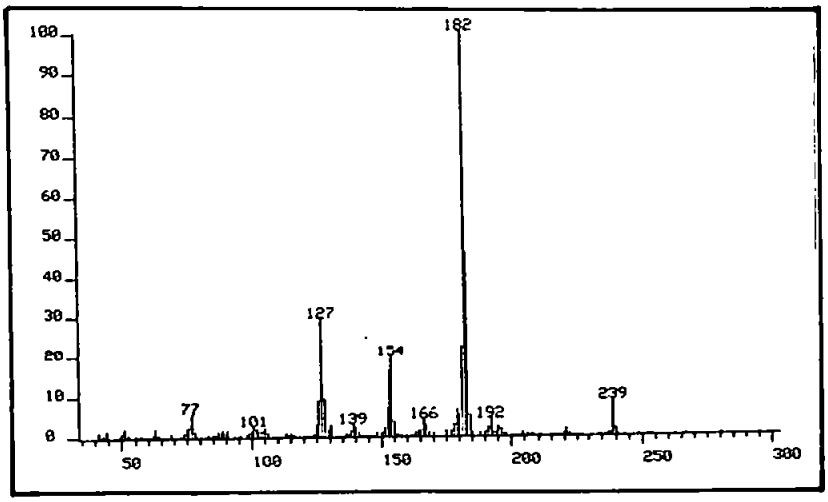


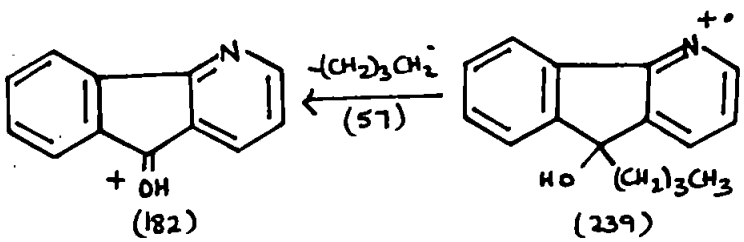


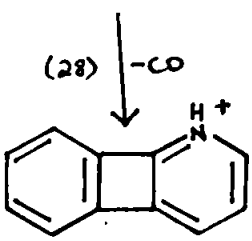
Appendix I.33i 5-butyl-5-hydoxy-indeno [1,2-b] pyridine (220)

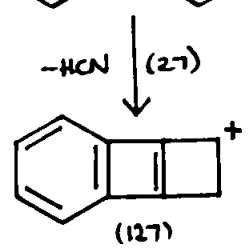


$C_{16}H_{17}NO$ RMM=239

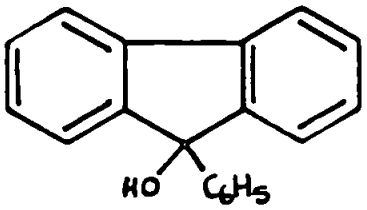




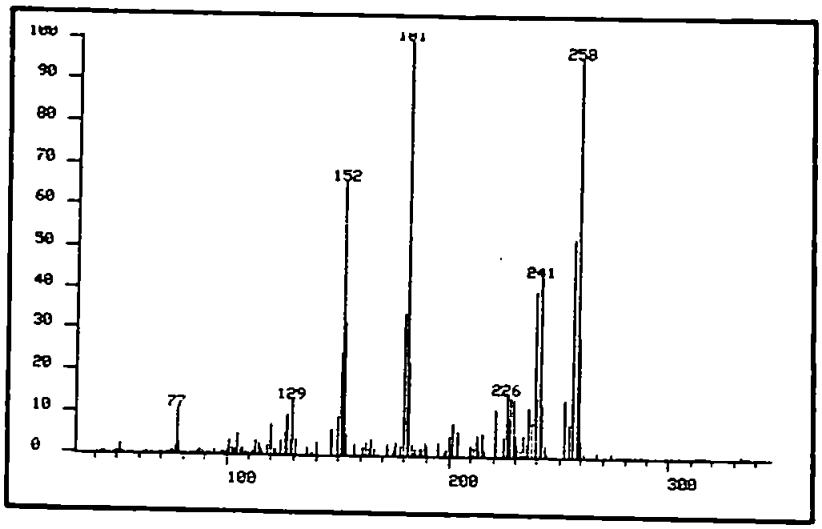


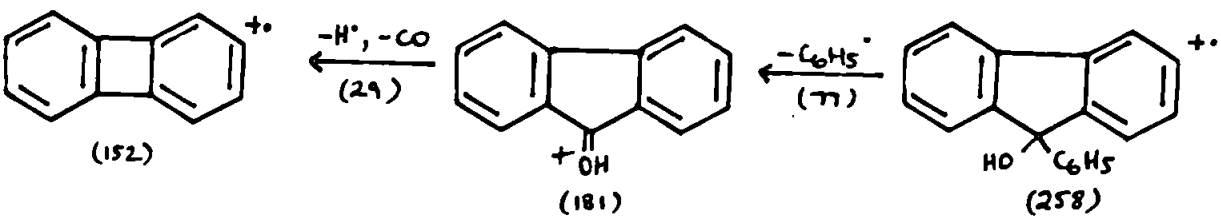


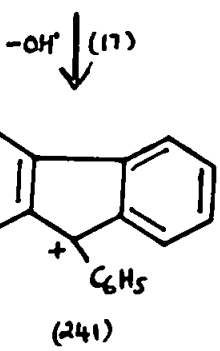
Appendix 1.34 9-hydroxy,9-phenylfluorene (223)



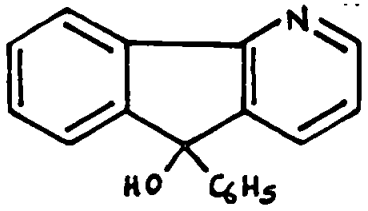
$C_{19}H_{14}O$ RMM=258



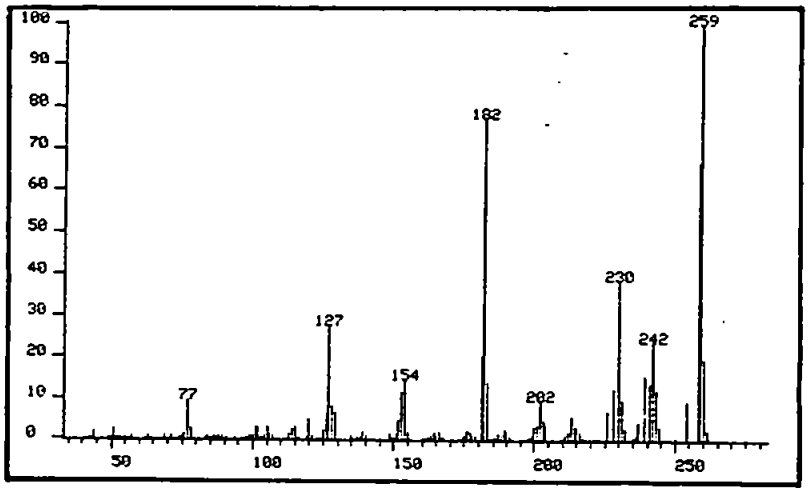


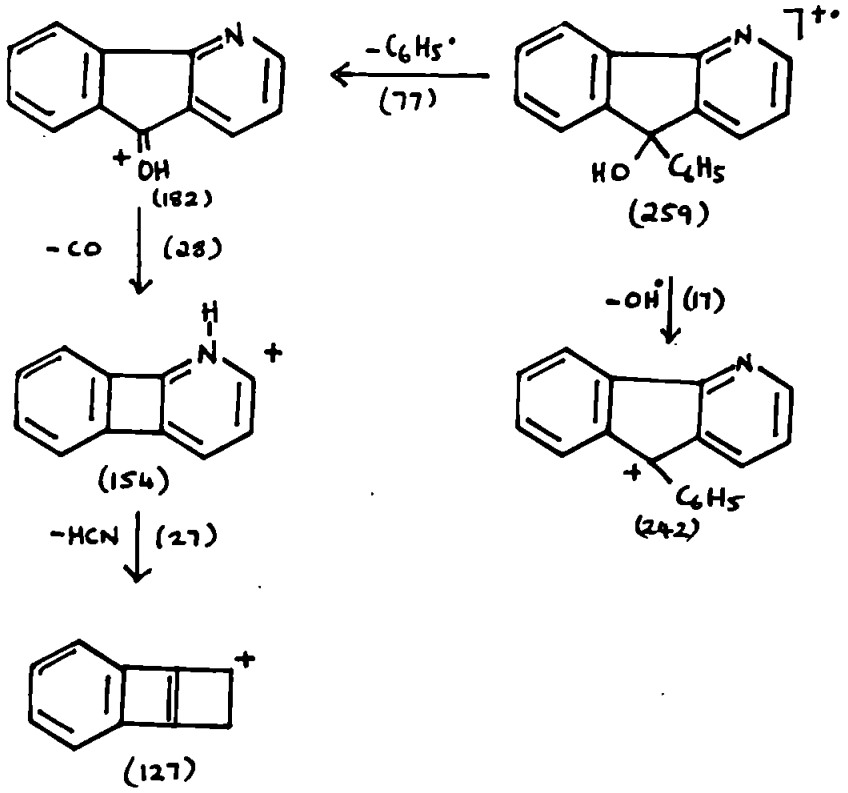


Appendix 1.35 5-hydroxy,5-phenylindeno [1,2-b] pyridine (222)

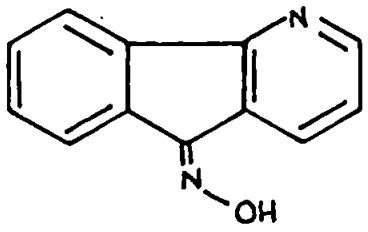


$C_{18}H_{13}NO$ RMM=259

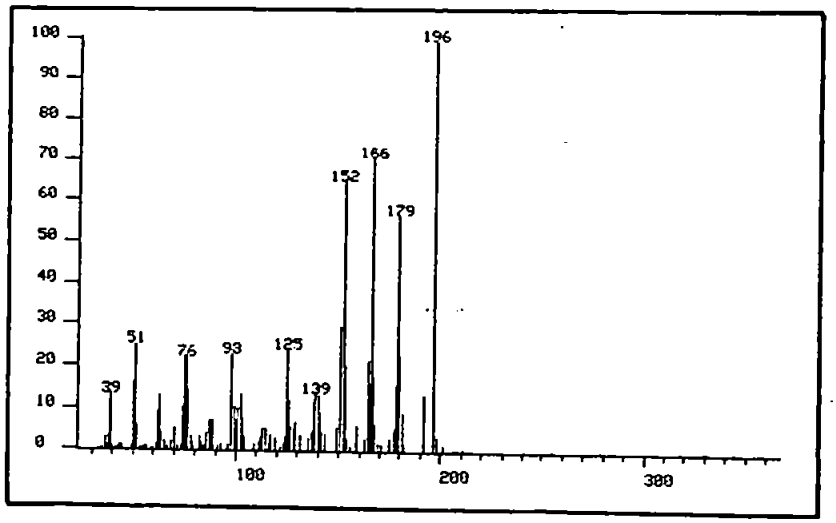


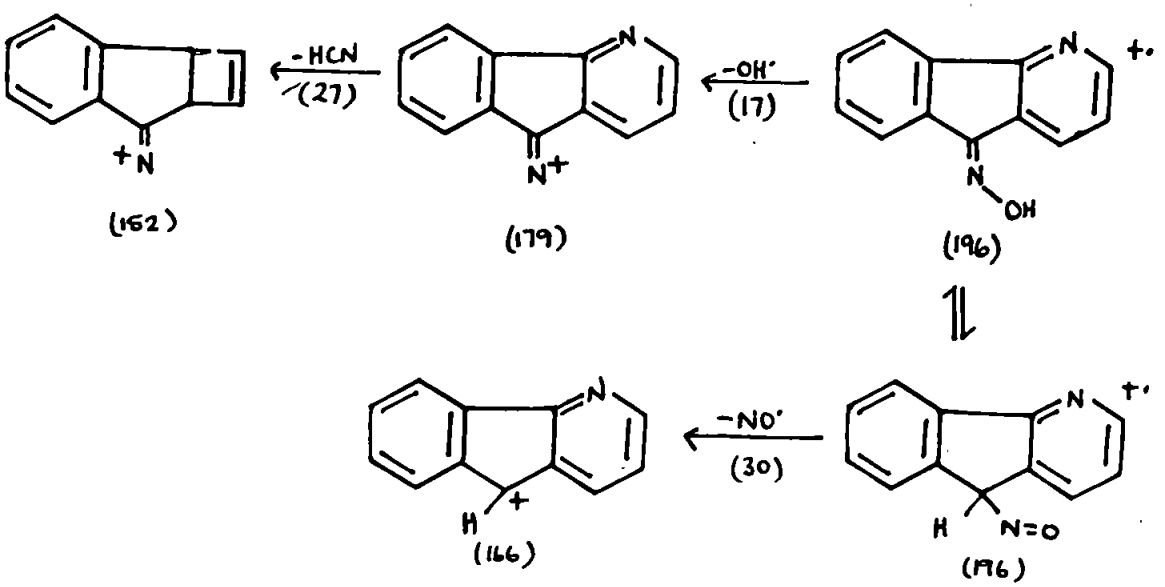


Appendix 1.36 5H-indeno [1,2-b] pyridine-5-one oxime (224)

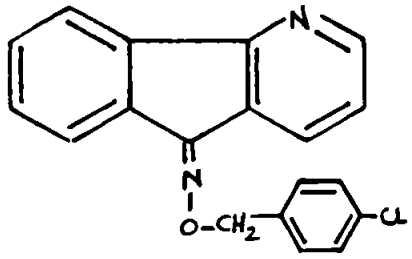


$C_{12}H_8N_2O$ RMM=196

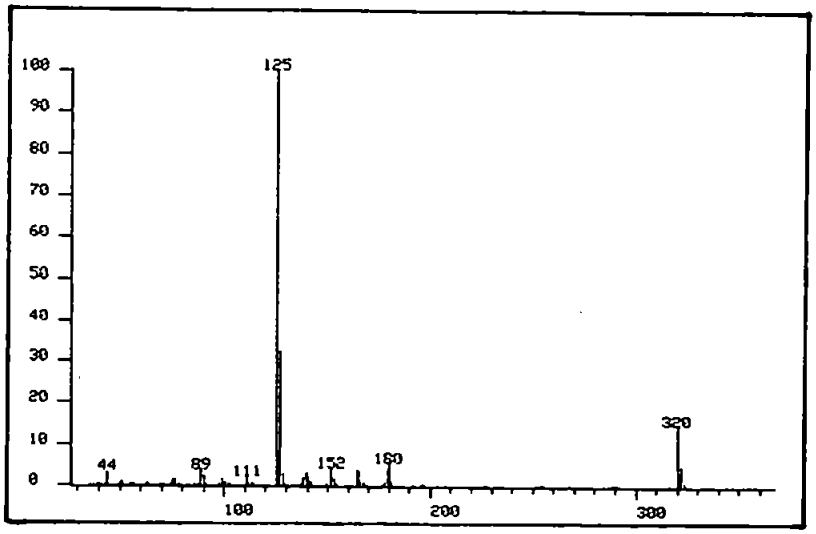


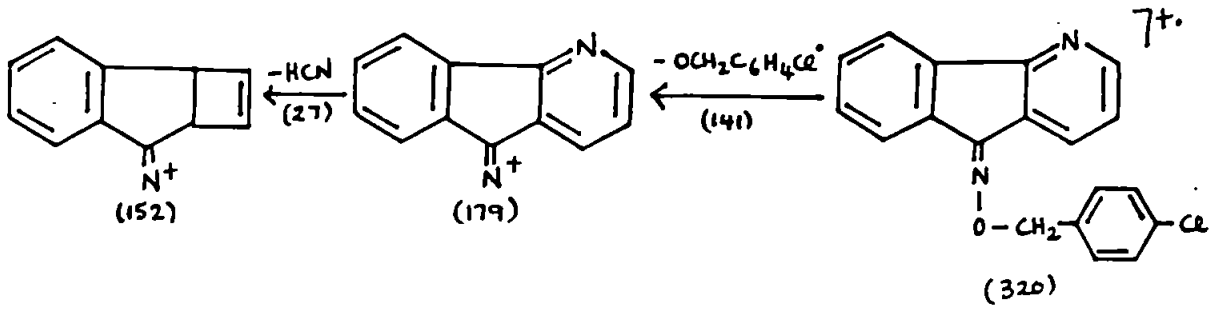


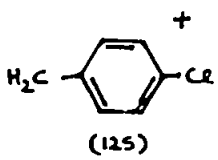
Appendix 1.37 5H-indeno[1,2-b]pyridine-5-one 4-chlorobenzyl -oxime (225)



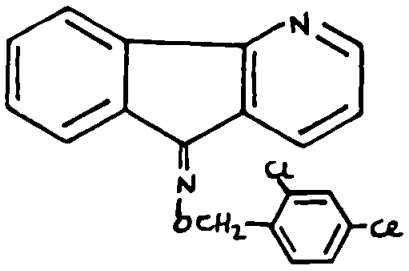
$C_{19}H_{13}H_2OCl$ RMM=320



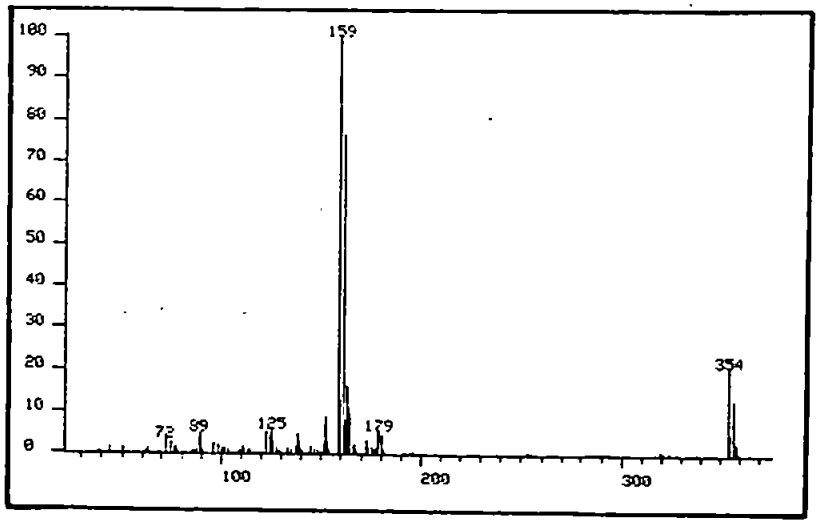


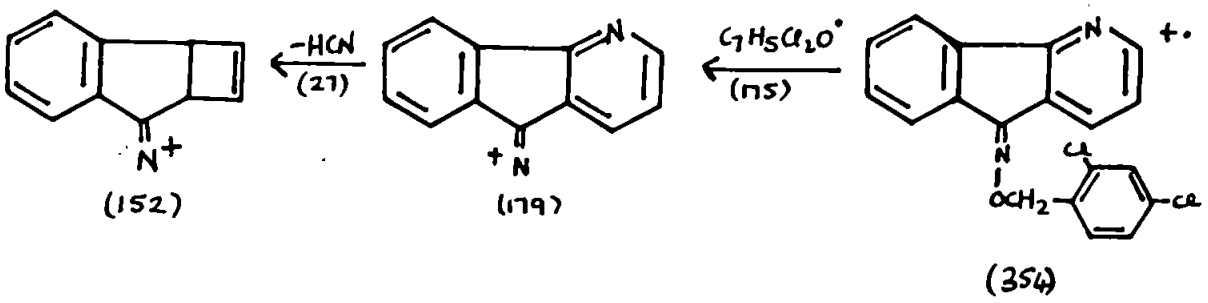


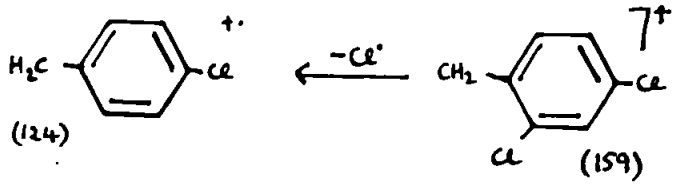
Appendix 1.38 5H-indeno [1,2-b] pyridine-5-one 2,4-dichloro-benzyl oxime (226)



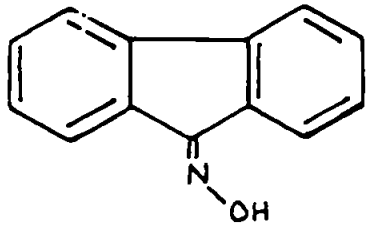
$C_{19}H_{12}N_2O\,Cl_2$ RMM=354



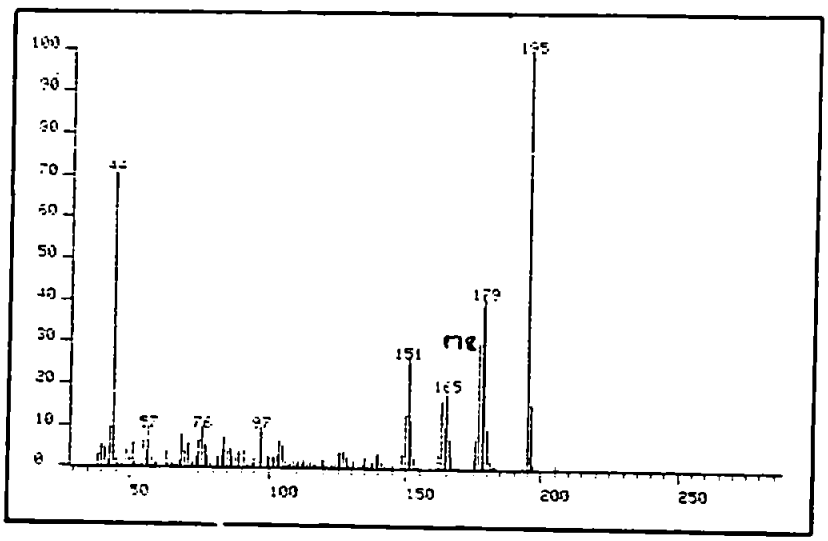


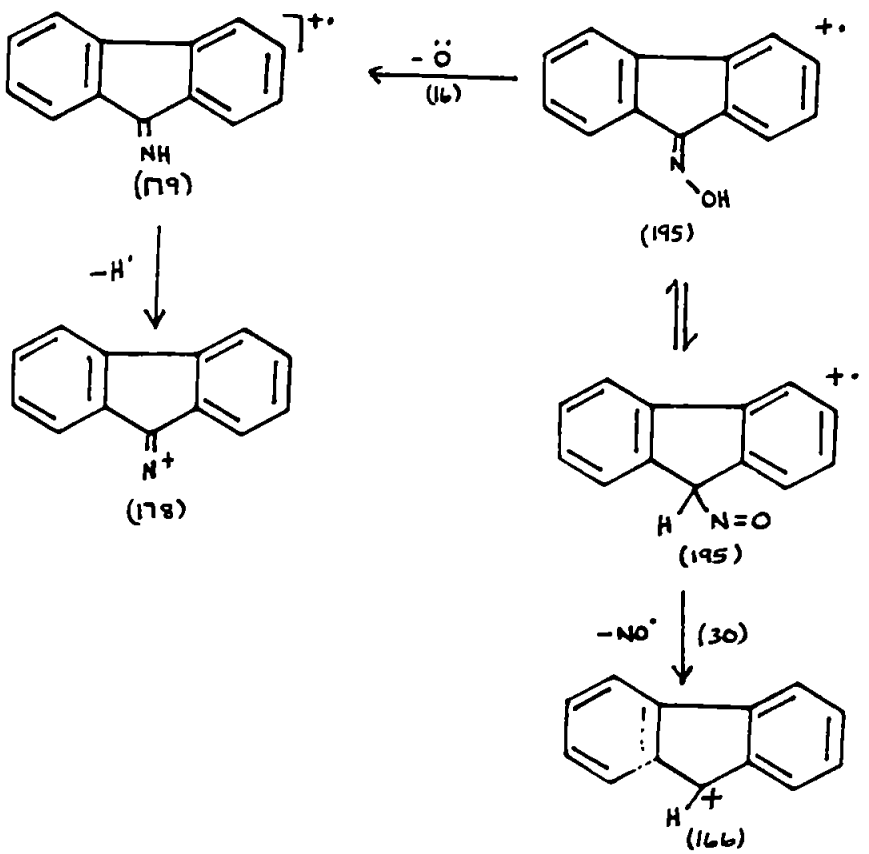


Appendix 1.39 Fluorenone oxime (227)

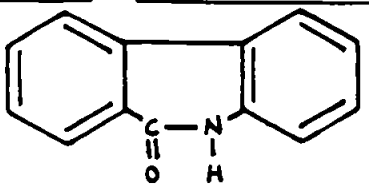


$C_{13}H_9NO$ RMM=195

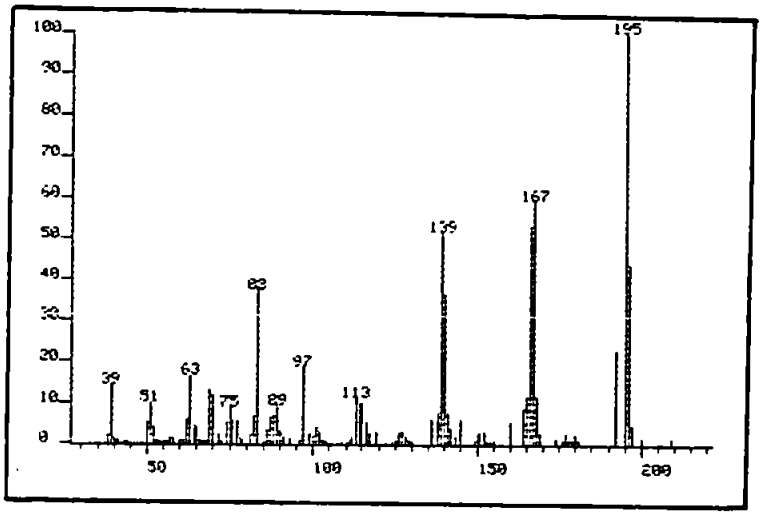


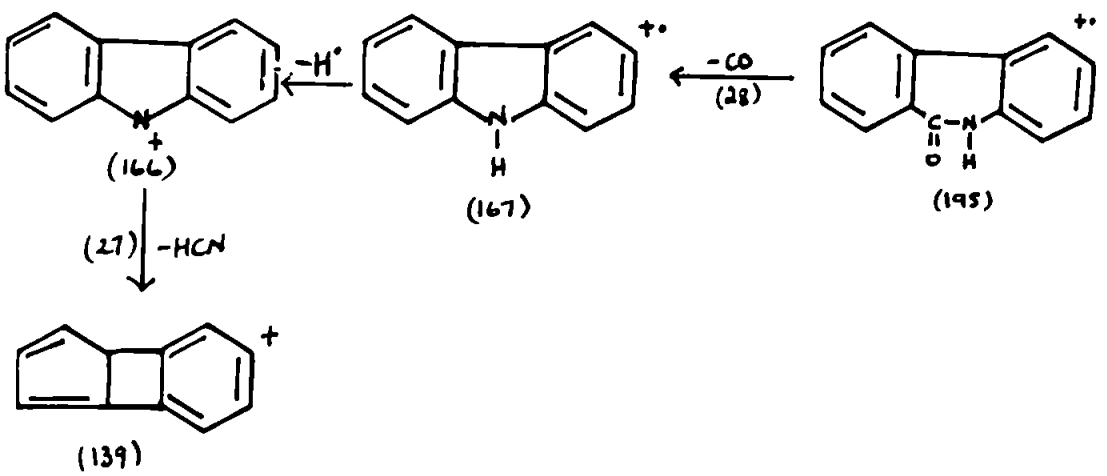


Appendix 1.40 6-phenanthridone (228)

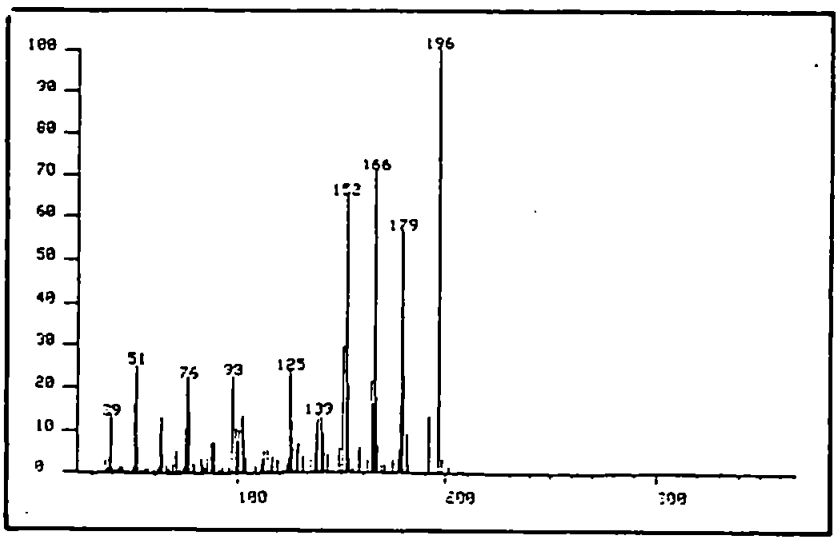


$C_{13}H_9NO$ RMM=195

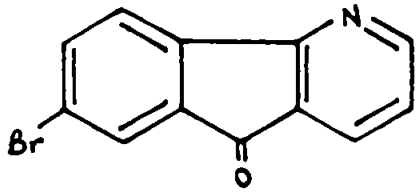




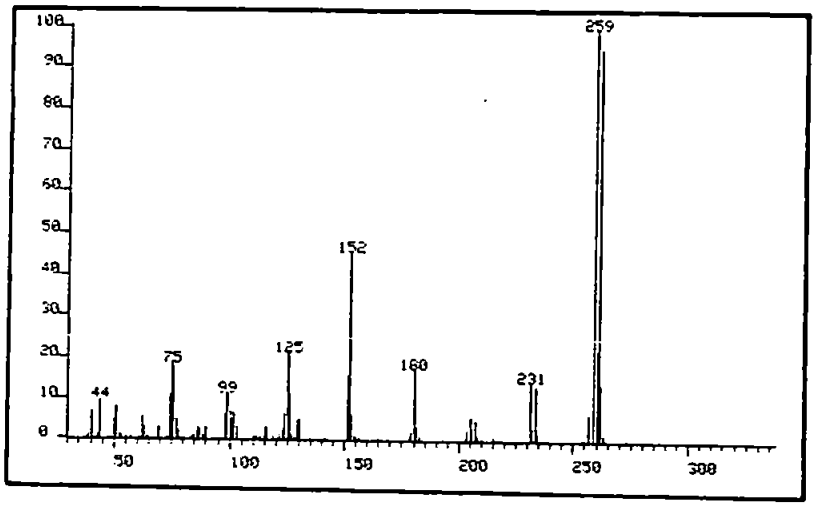
Appendix I.41 Attempted Beckmann Rearrangement of (224)

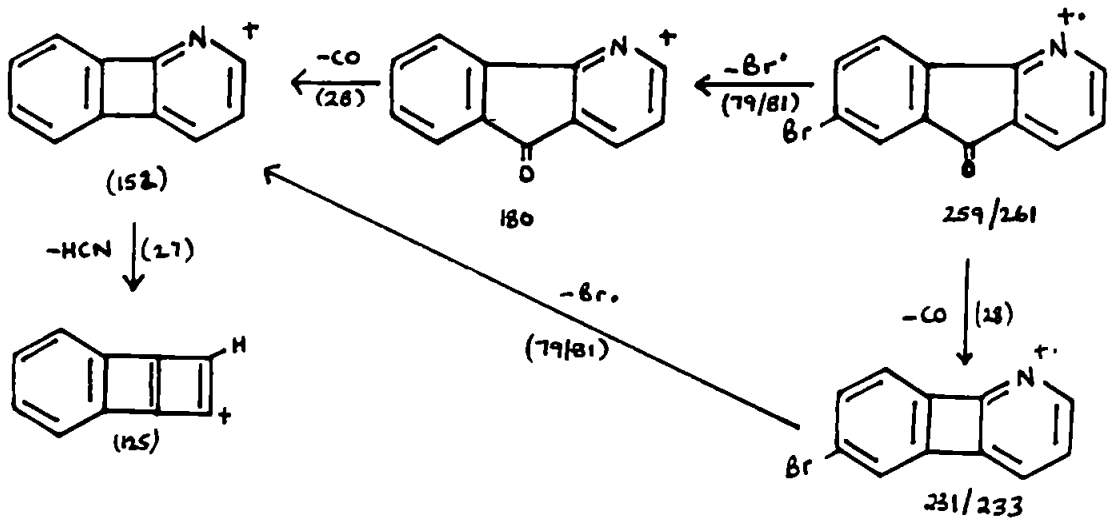


Appendix 1.42 7-bromo-5H-indeno[1,2-b]pyridin-5-one (233)

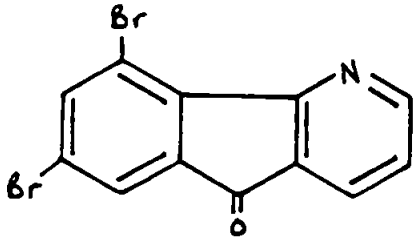


$C_{12}H_6NOBr$ RMM=259/261

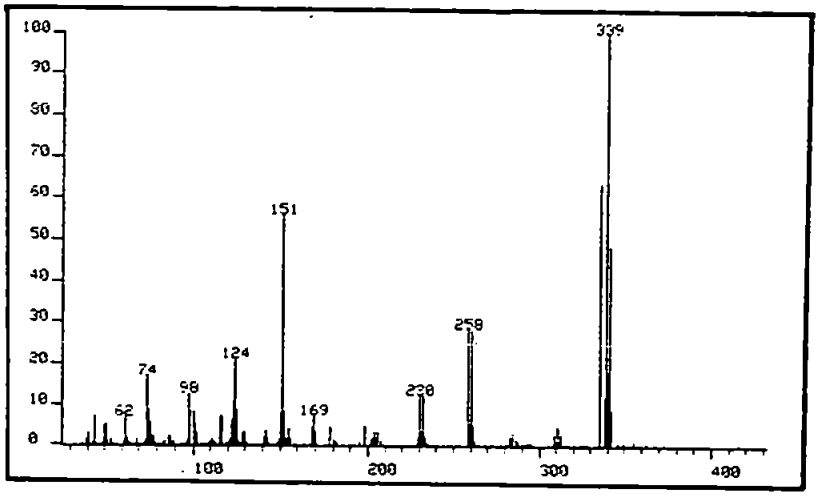


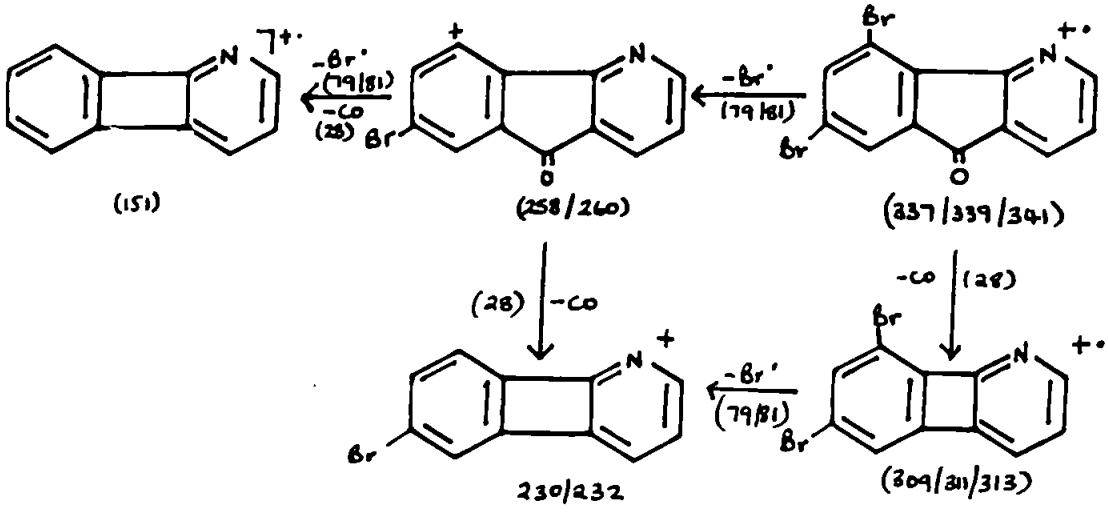


Appendix 1.43 7,9-dibromo-5H-indeno[1,2-b]pyridin-5-one (234).

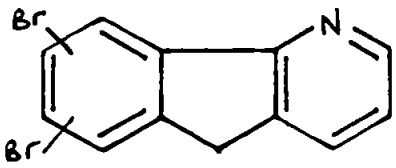


$C_{12}H_5NOBr_2$ RMM=337/339/341

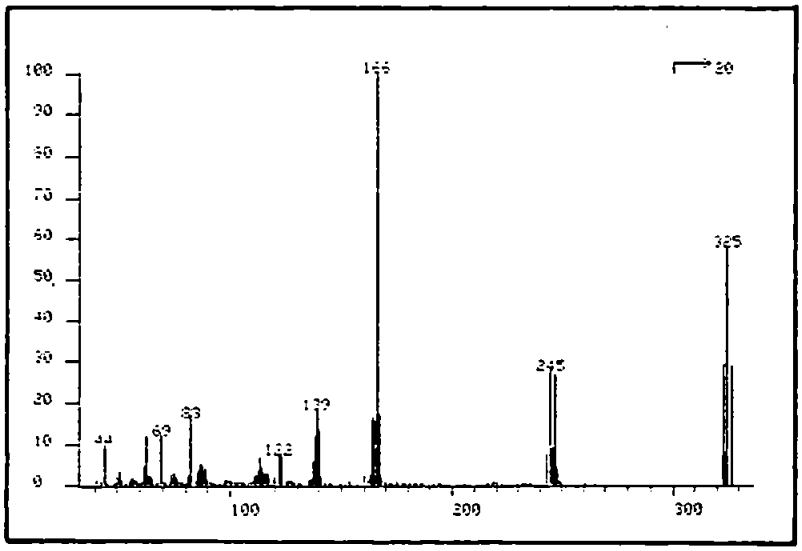


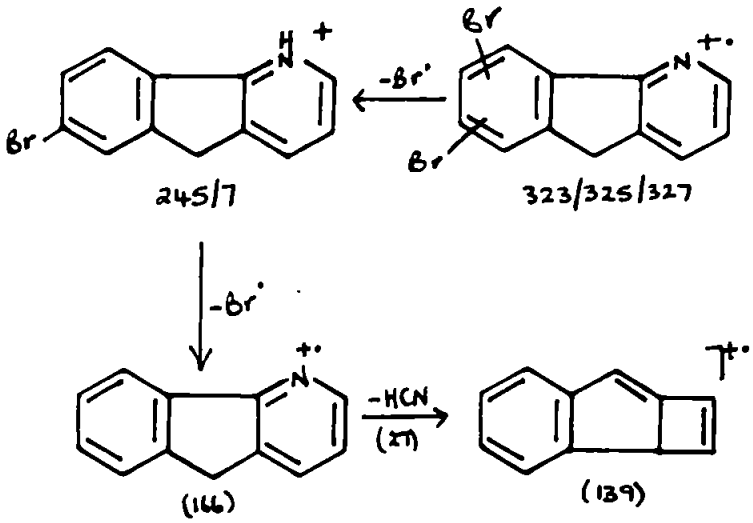


Appendix 1.44 Dibromo-5H-indeno[1,2-b]pyridine (235)

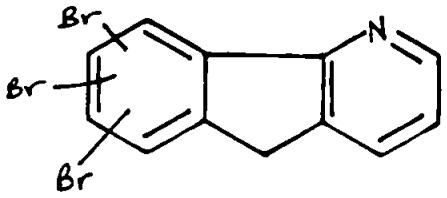


$C_{12}H_7NBr_2$ 323/325/327

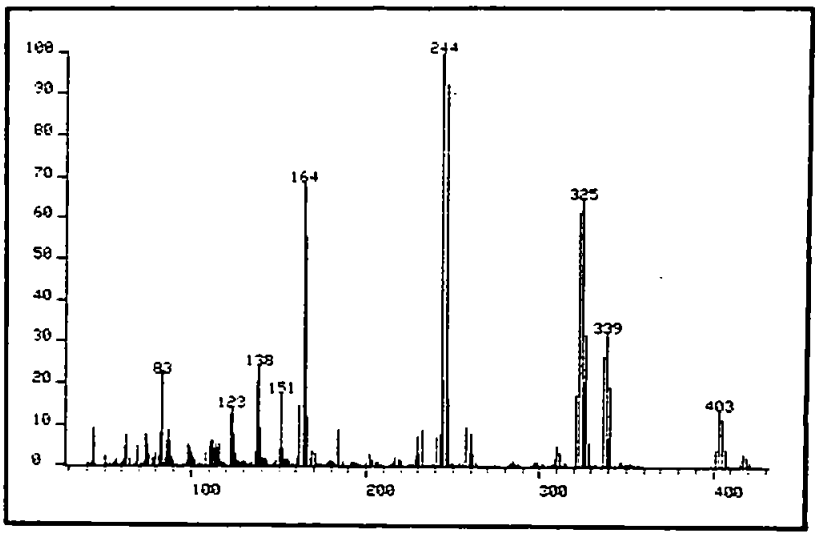


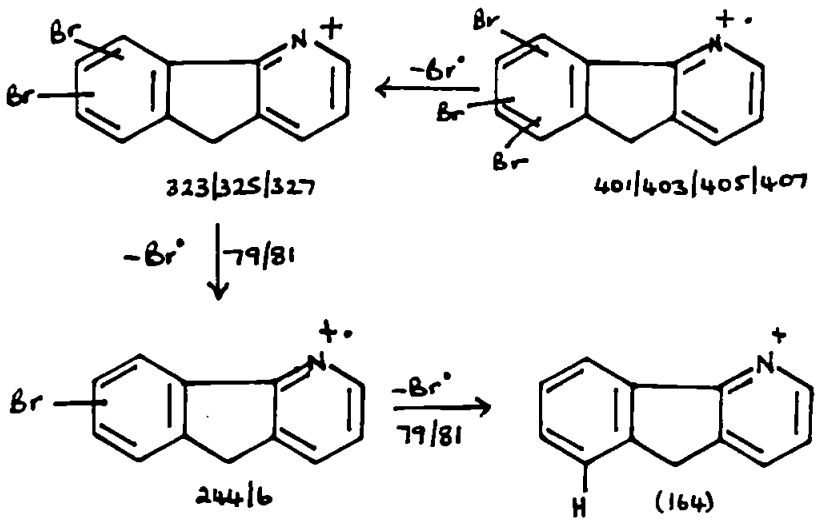


Appendix 1.45 Tribromo-5H-indeno[1,2-b]pyridine (236)

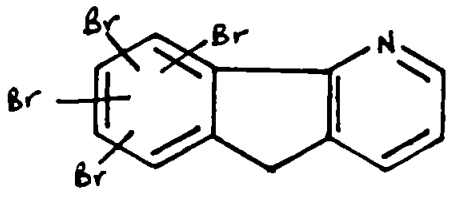


$C_{12}H_6NBr_3$ RMM=401/403/405/407

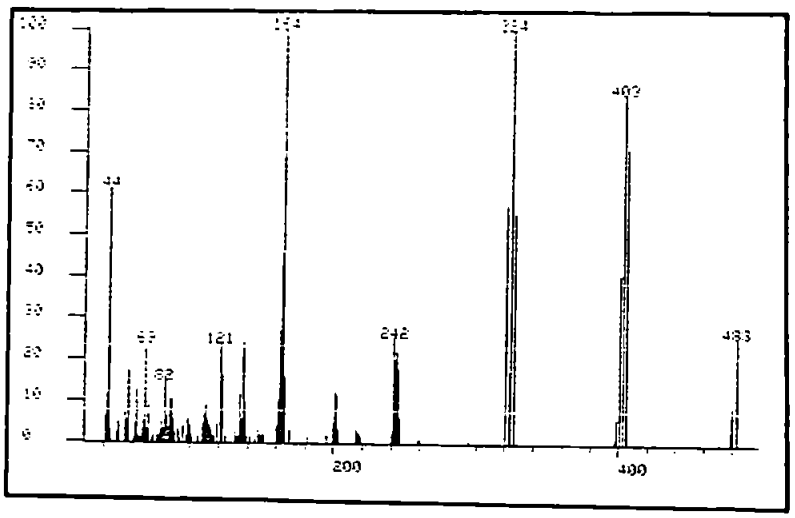


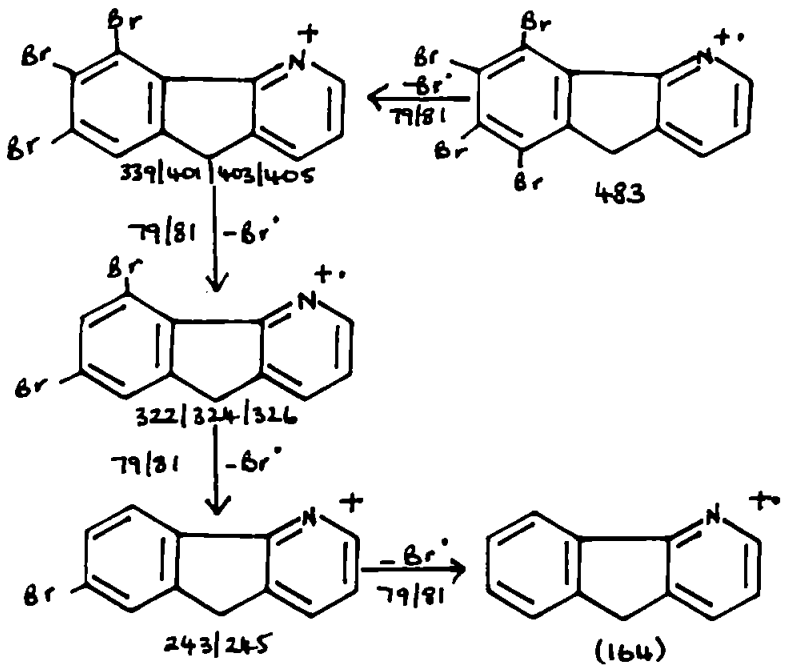


Appendix 1.46 Tetrabromo-5H-indeno[1,2-b]pyridine (237)

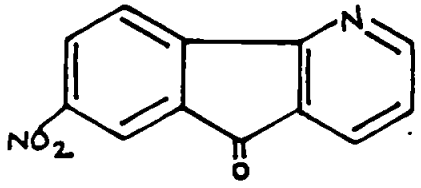


$C_{12}H_5NBr_4$ RMM=479/481/483/485

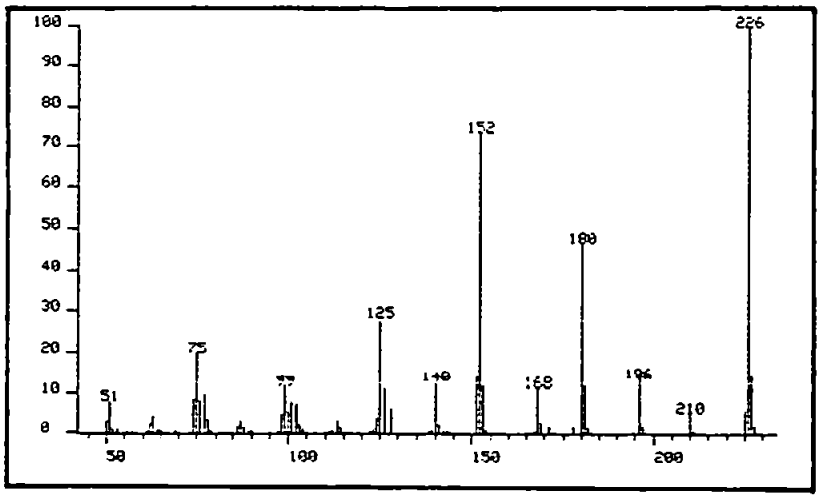


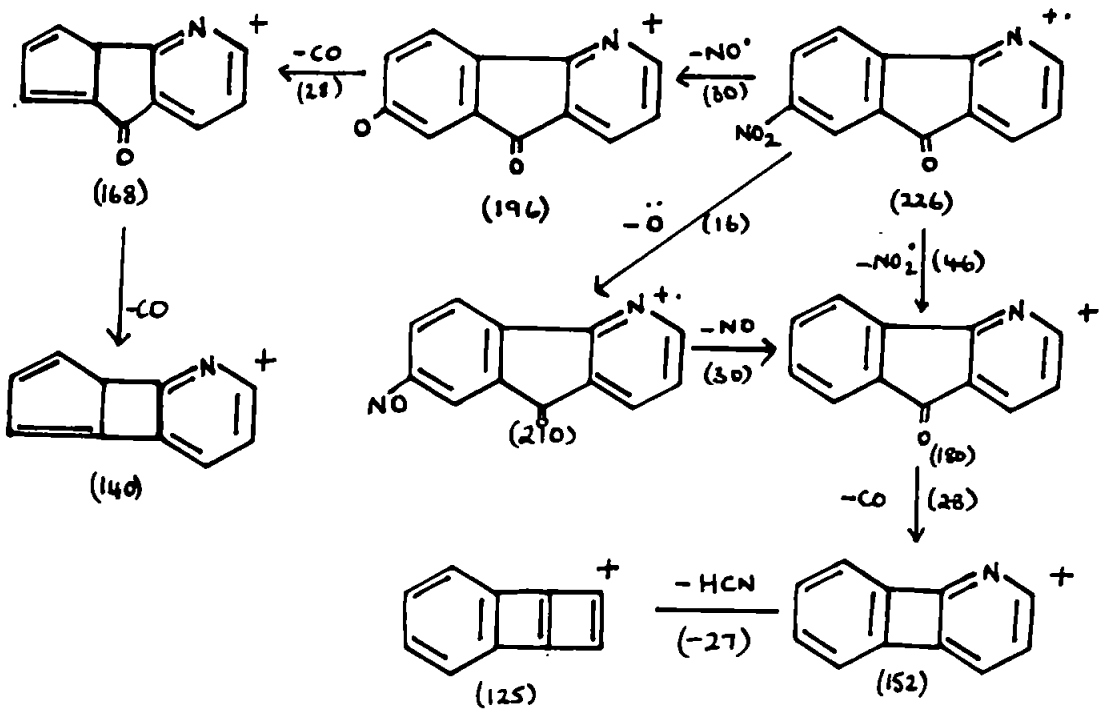


Appendix 1.47 7-nitro-5H-indeno[1,2-b]pyridin-5-one (238)

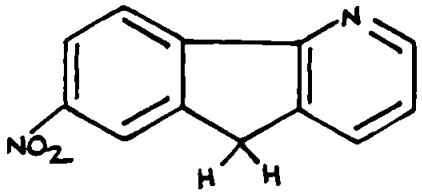


$C_{12}H_6N_2O_3$ RMM=226

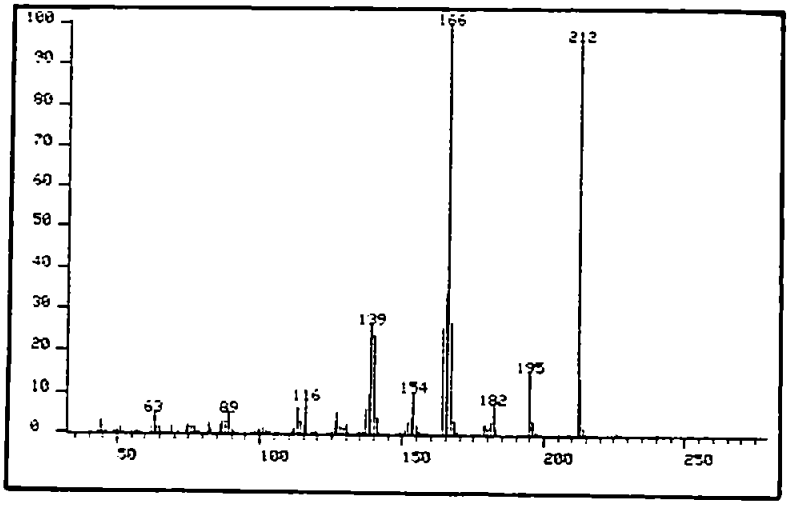


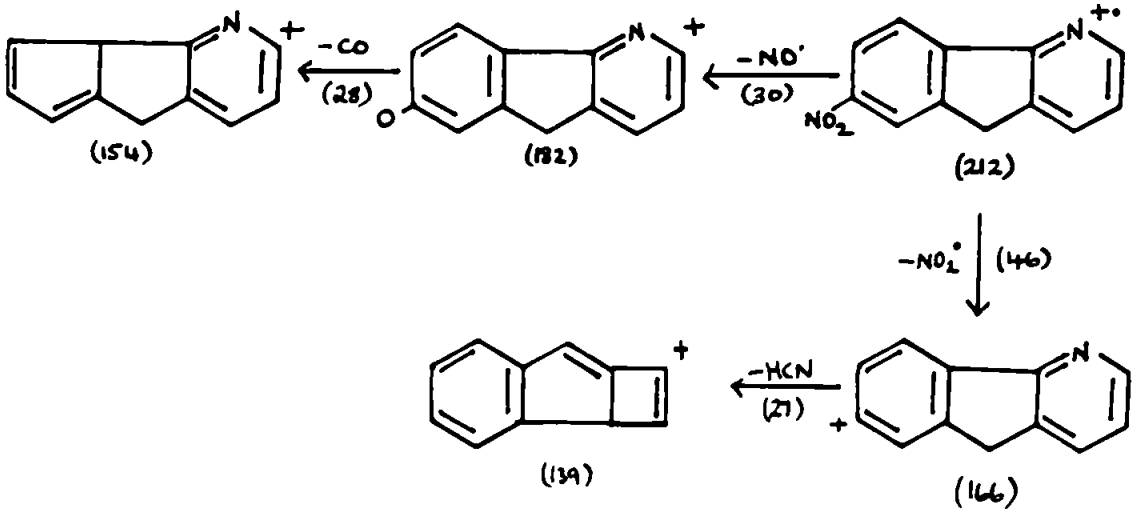


Appendix 1.48 7-nitro-5H-indeno[1,2-b]pyridine (239)

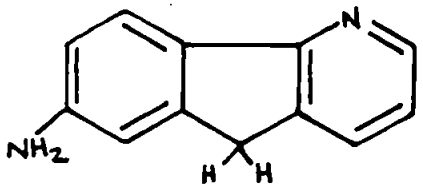


$C_{12}H_8N_2O_2$ RMM=212

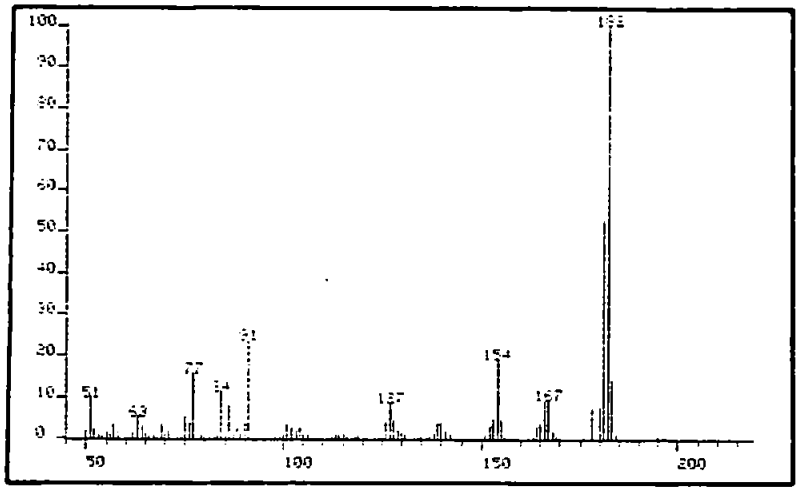


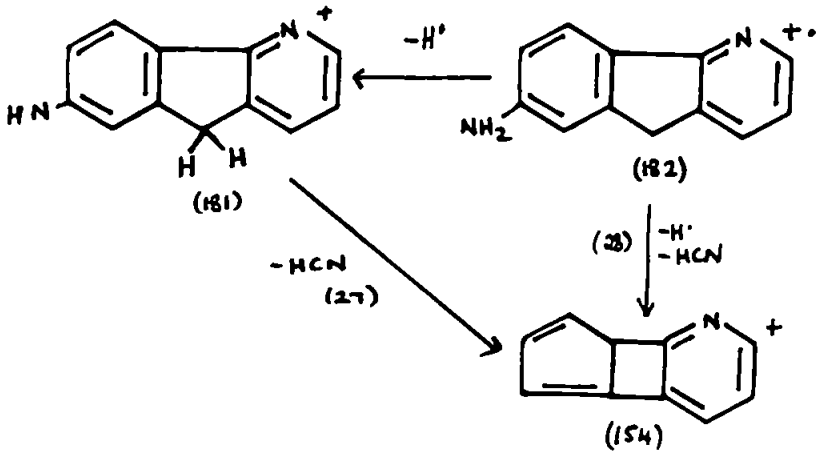


Appendix 1.49 7-amino-5H-indeno[1,2-b]pyridine (240)

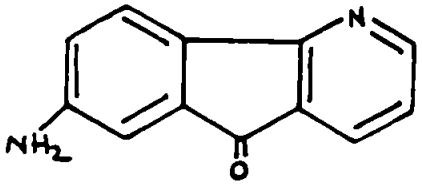


$C_{12}H_{10}N_2$ RMM=182

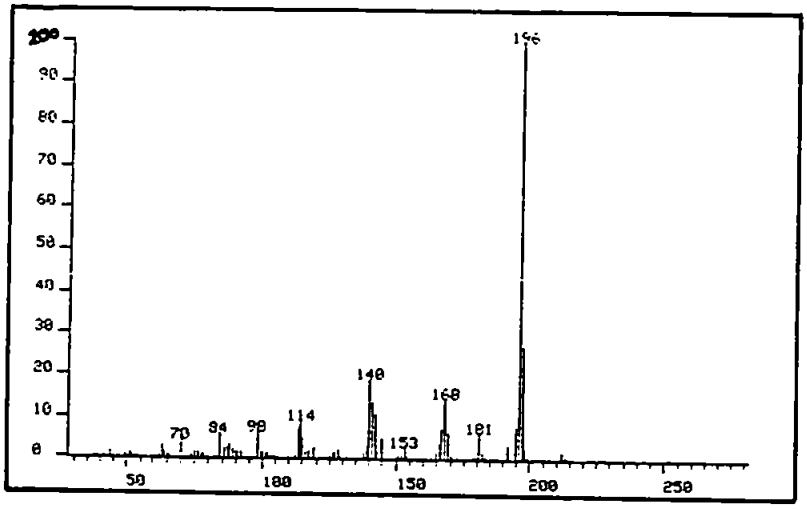


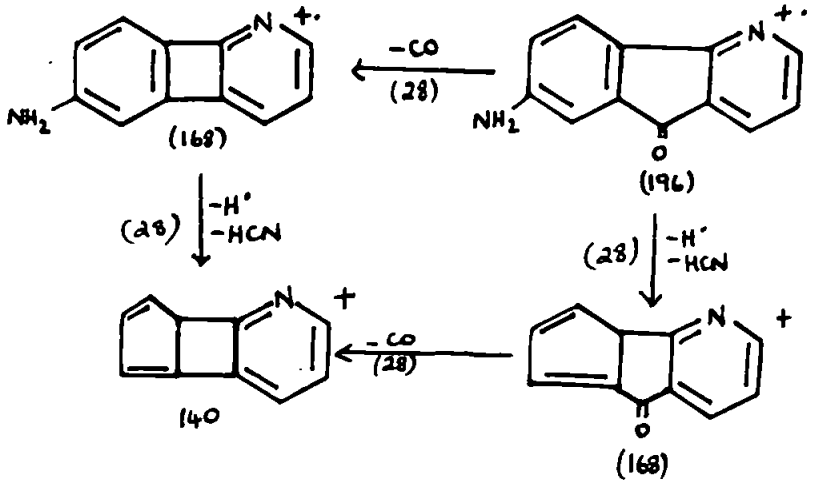


Appendix 1.50 7-amino-5H-indeno [1,2-b] pyridin-5-one (241)



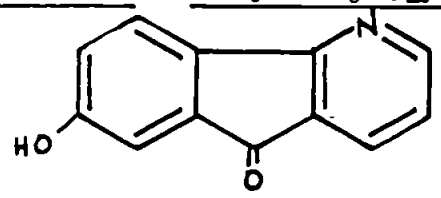
$C_{12}H_8N_2O$ RMM=196



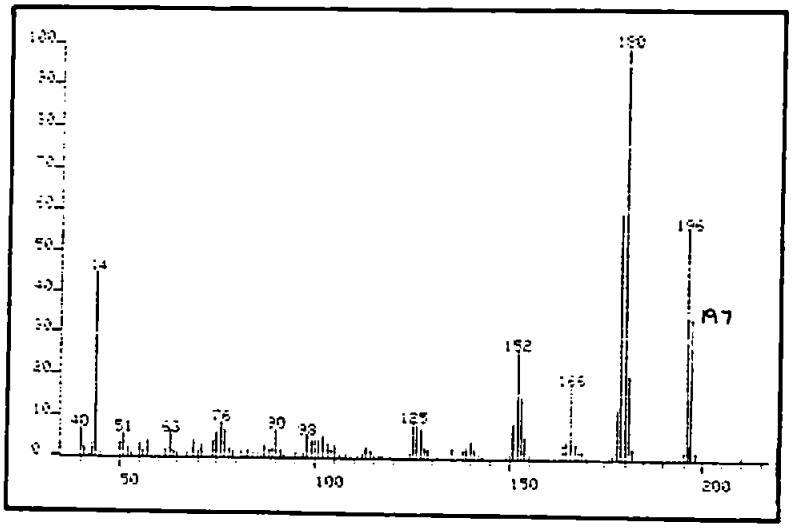


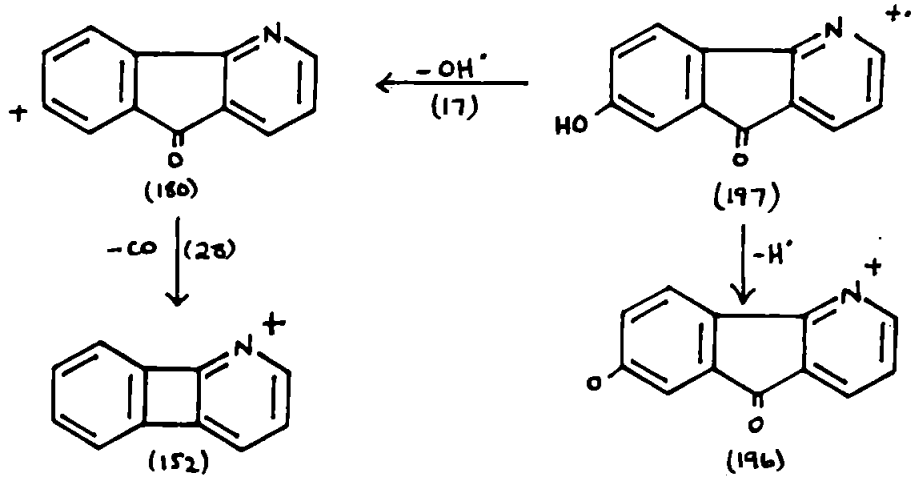
Appendix 1.51 7-hydroxy-5H-indeno[1,2-b]pyridin-5-one

(242)

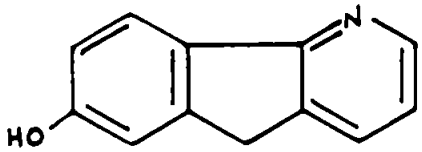


$C_{12}H_7NO_2$ RMM=197

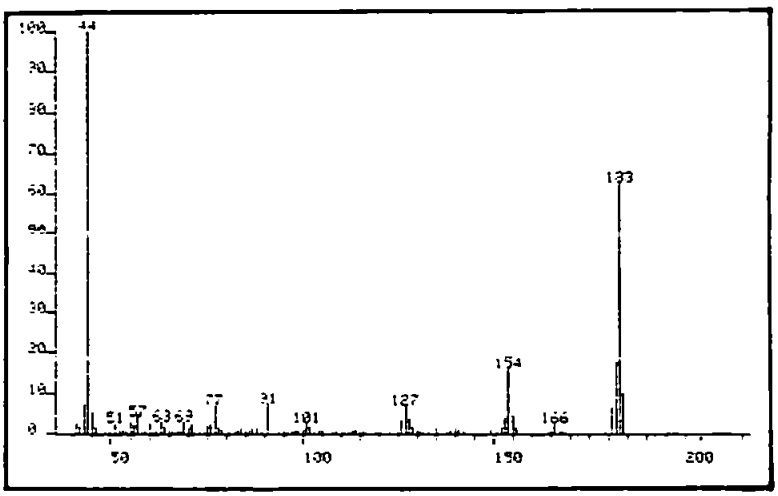


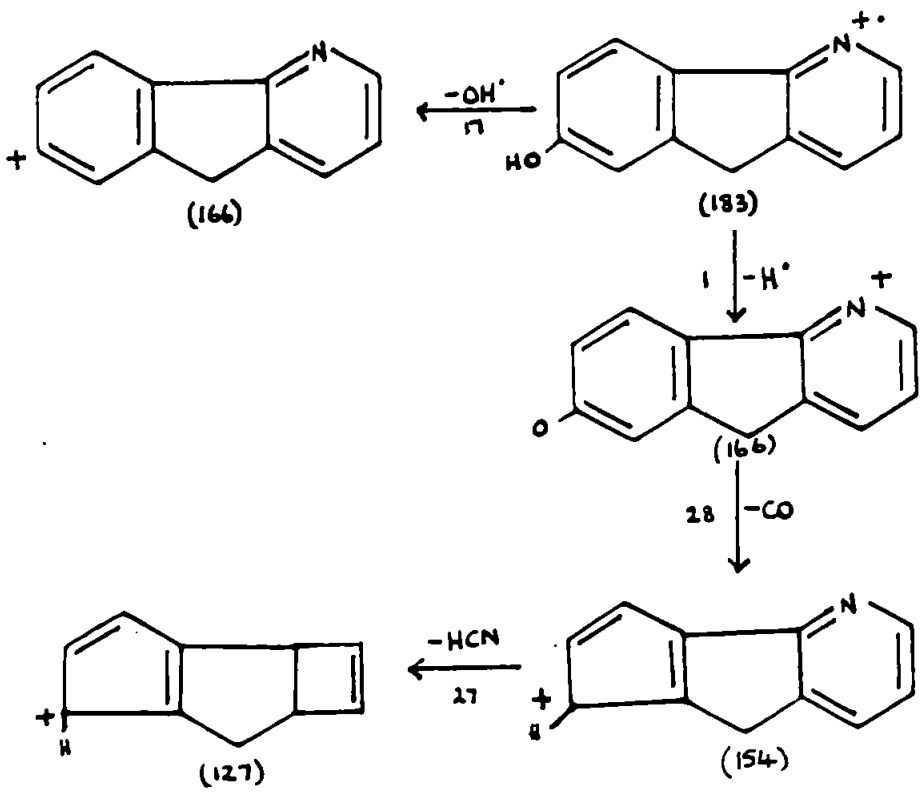


Appendix I.52 7-hydroxy-5H-indeno [1,2-b] pyridine (243)

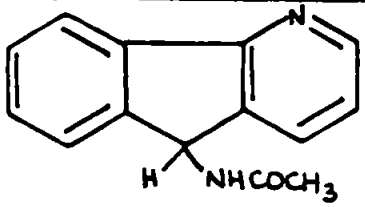


$C_{12}H_9NO$ RMM=183

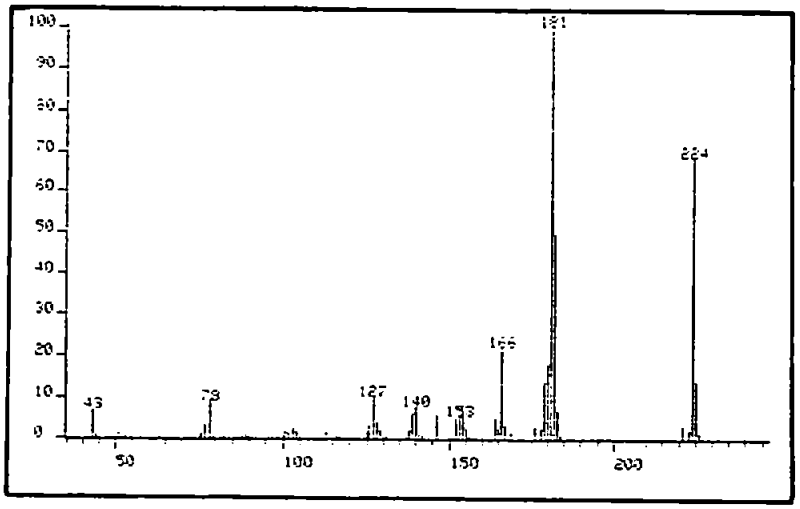


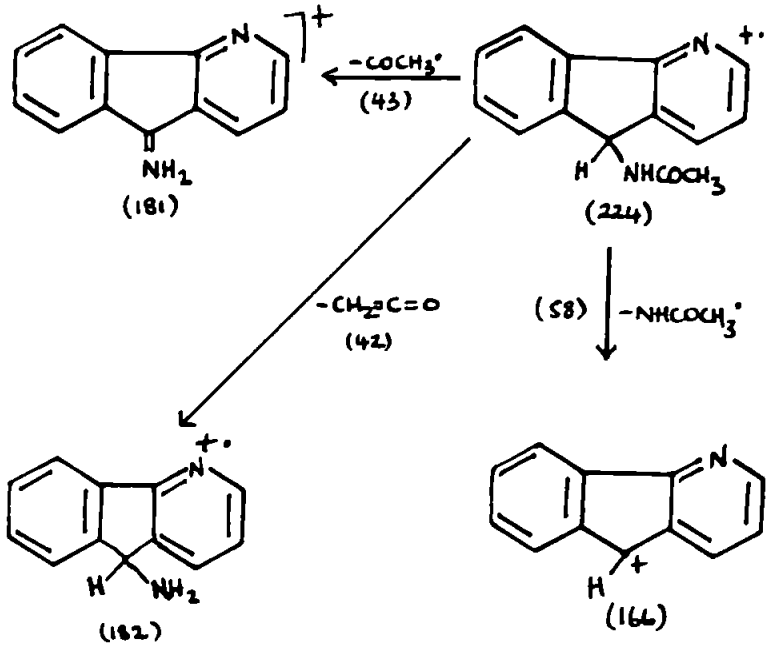


Appendix 1.53 5-acetamido,5H-indeno[1,2-b]pyridine (230)

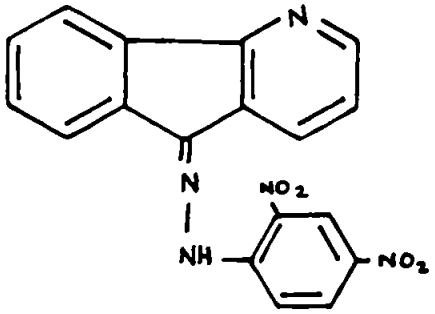


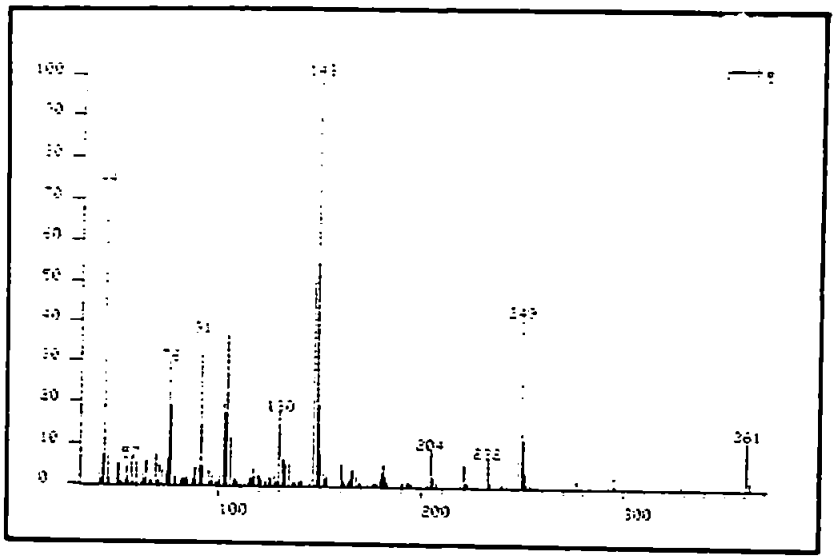
$C_{14}H_{12}N_2O$ RMM=224





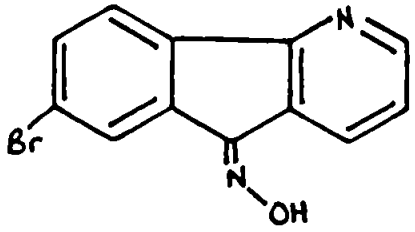
Appendix 1.54 5H-indeno[1,2-b]pyridine 2,4-dinitrophenyl-hydrazone (231)



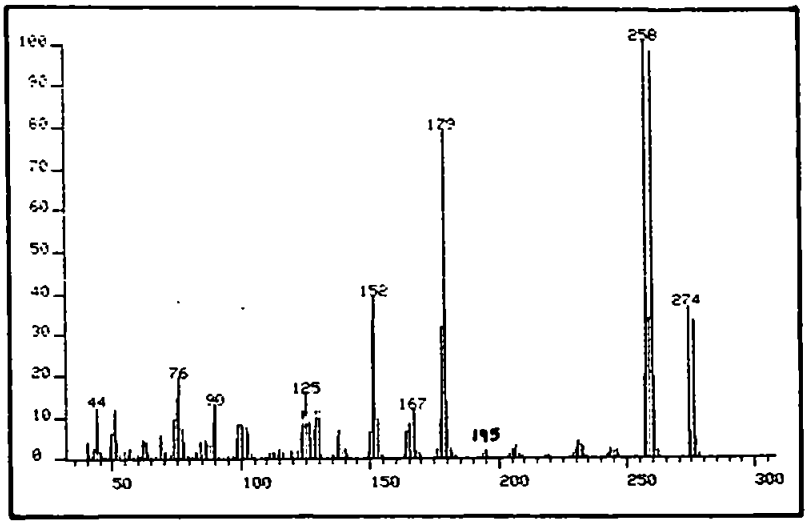


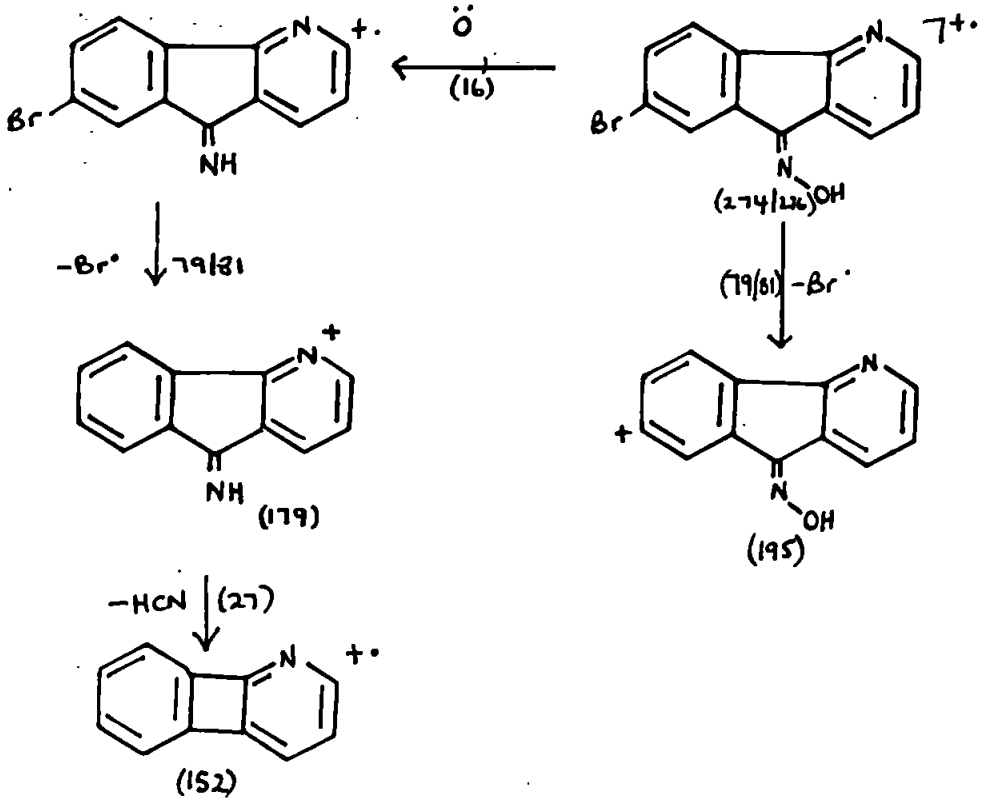
Appendix 1.55 7-bromo-5H-indeno[1,2-b]pyridine-5-one oxime

(244)

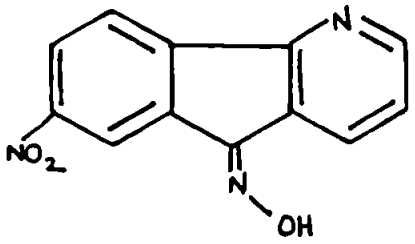


$C_{12}H_7N_2OBr$ RMM=274/276

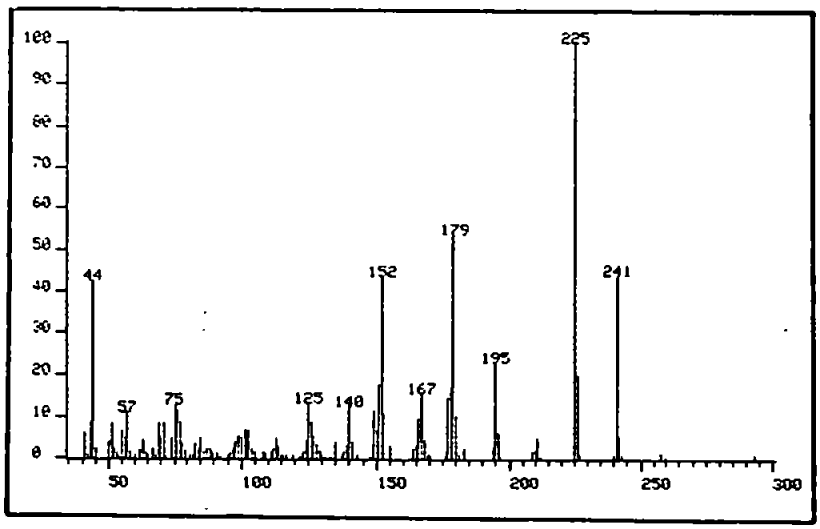


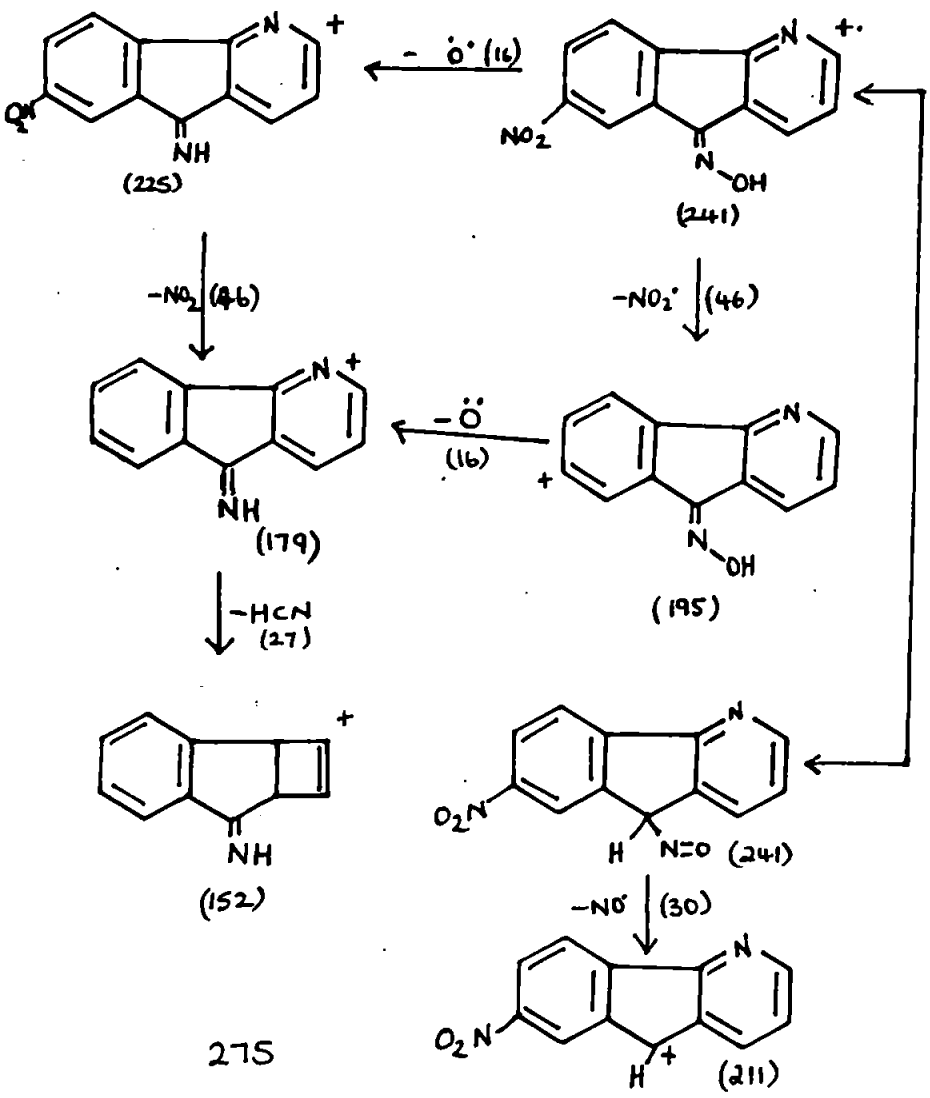


Appendix 1.56 7-nitro,5H-indeno[1,2-b]pyridine-5-one oxime (245)

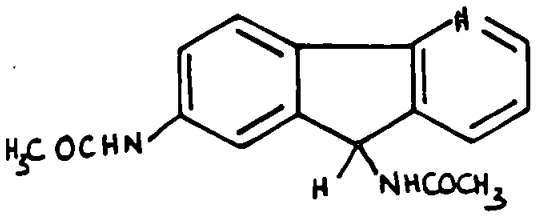


$C_{12}H_7N_3O_3$ RMM=241

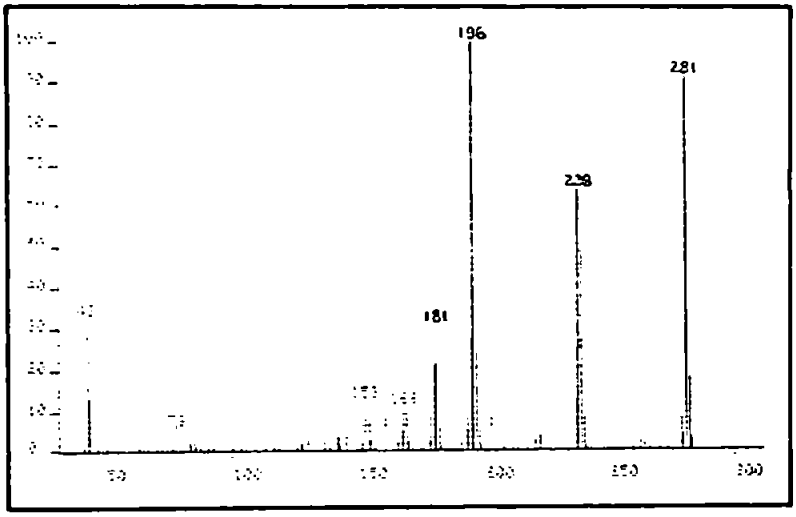


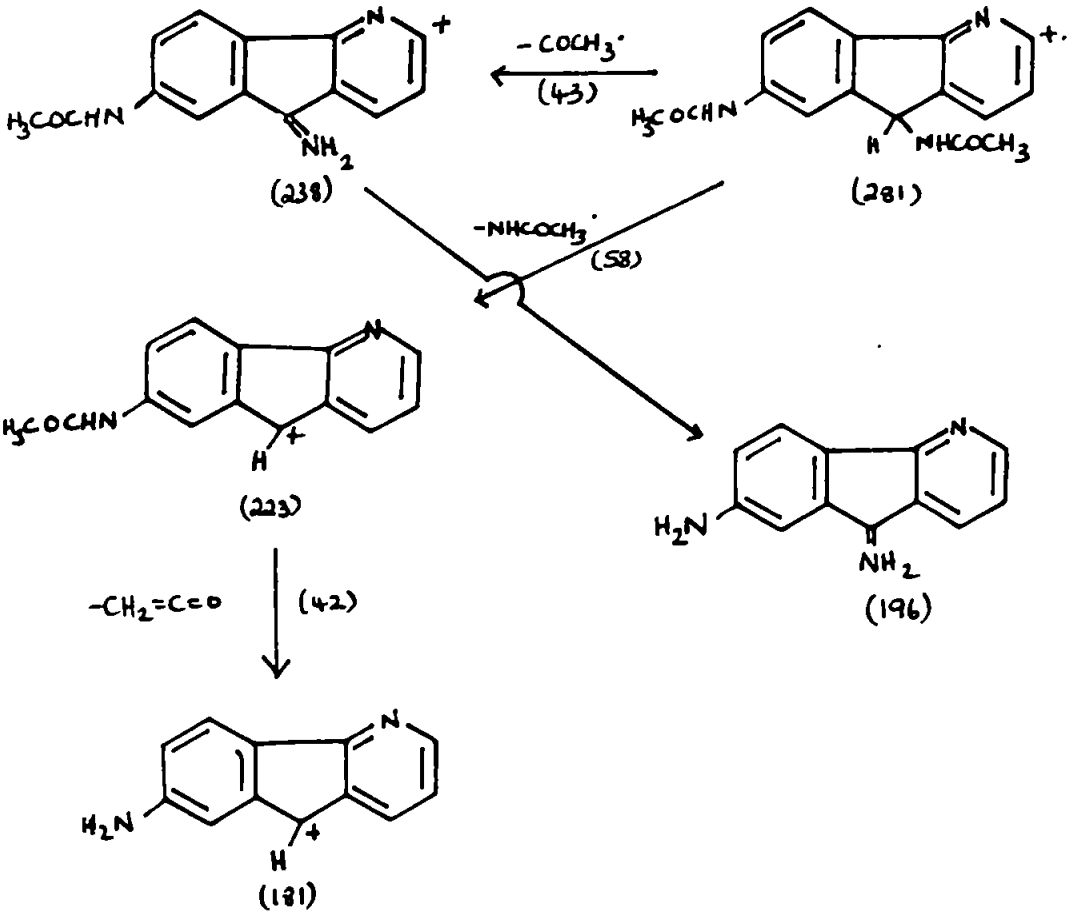


Appendix 1.57 5,7-diacetamido-5H-indeno[1,2-b]pyridine (246)

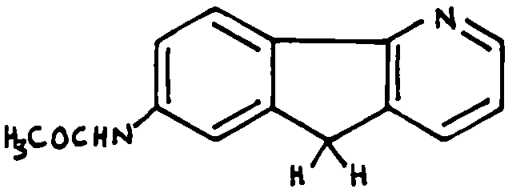


$C_{16}H_{15}N_3O_2$ RMM=281

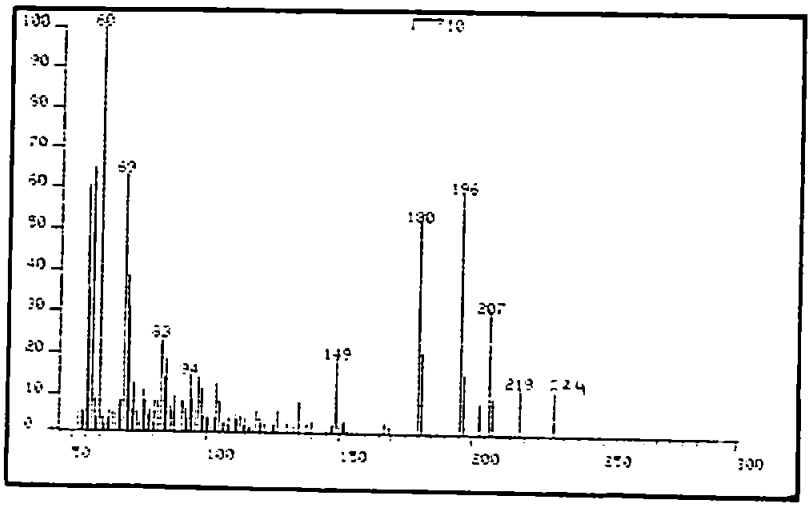


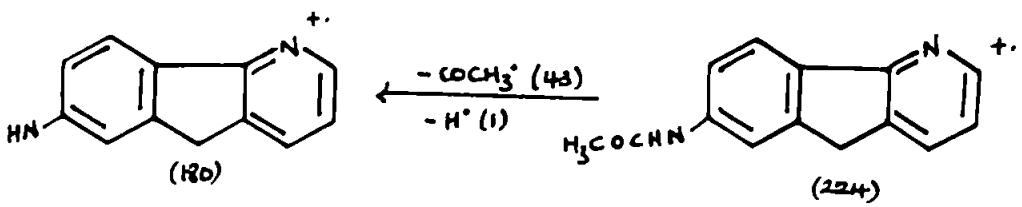


Appendix 1.58 7-ecetamido,5H-indeno [1,2-b] pyridine (247)

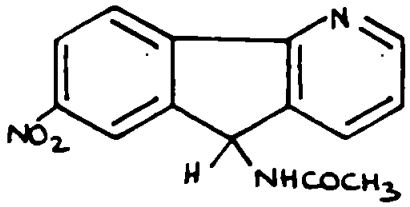


$C_{14}H_{12}N_2O$ RMM= 224

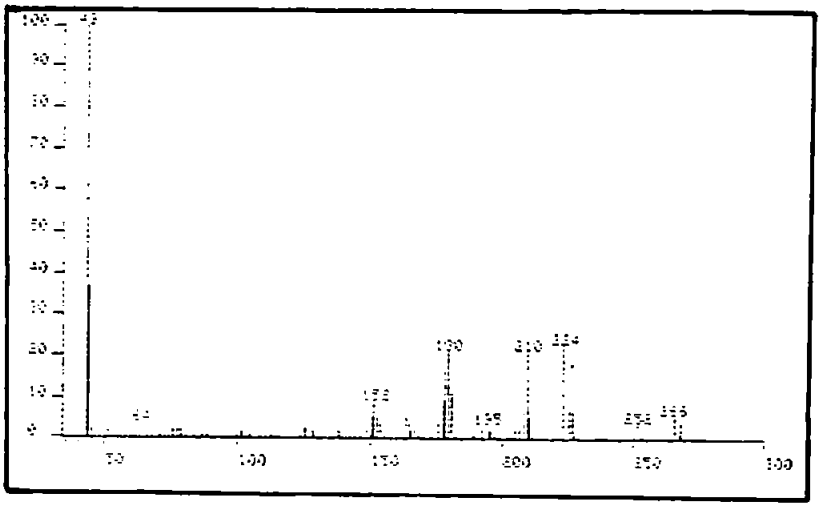


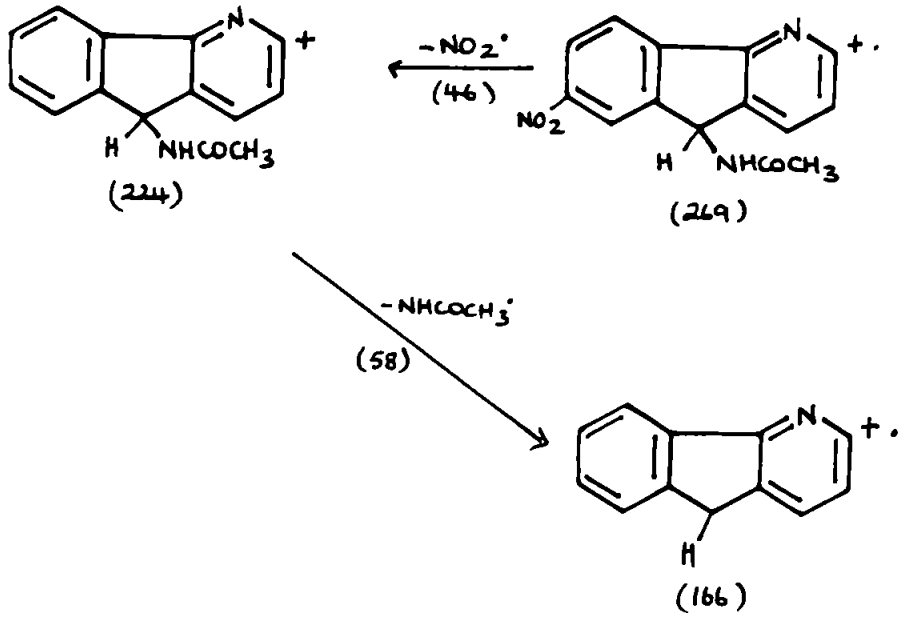


Appendix 1.59 5-acetamido,7-nitro-5H-indeno [1,2-b] pyridine (248)



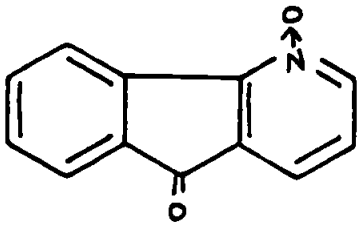
$C_{12}H_{11}N_3O_3$ RMM=269



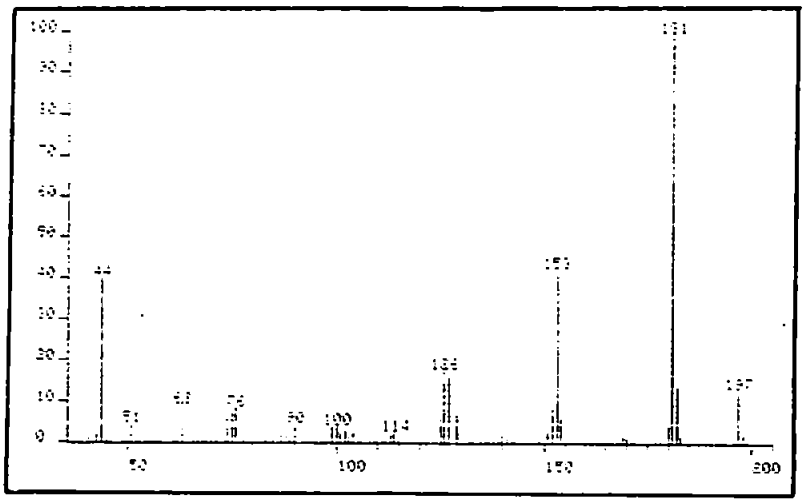


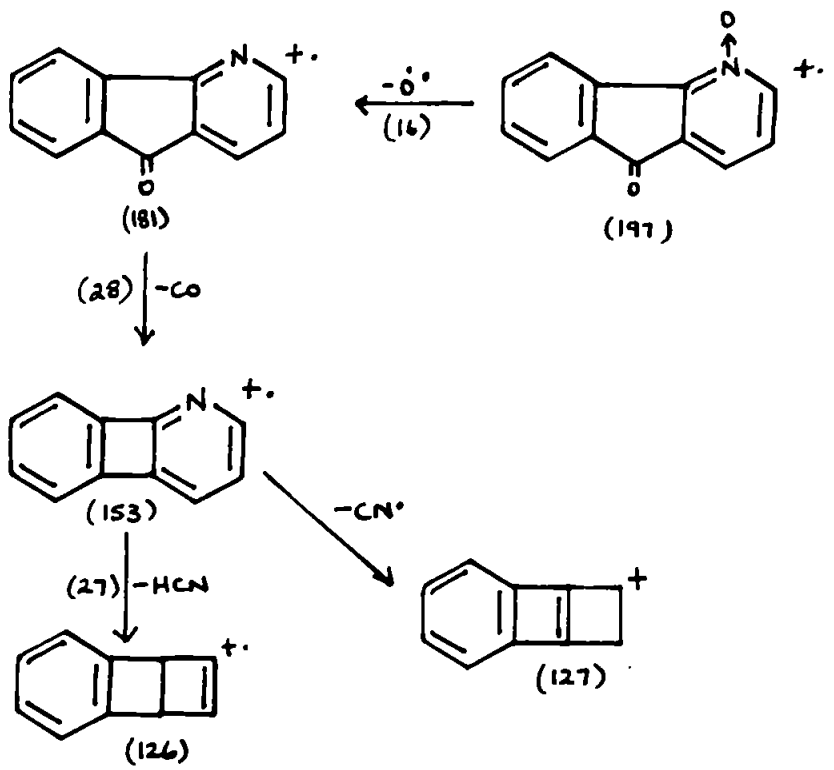
(224) (249) (166)

Appendix 1.60 5H-indeno[1,2-b]pyridin-5-one N-oxide (249)

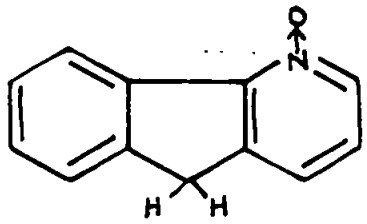


$C_{12}H_7NO_2$ RMM=197

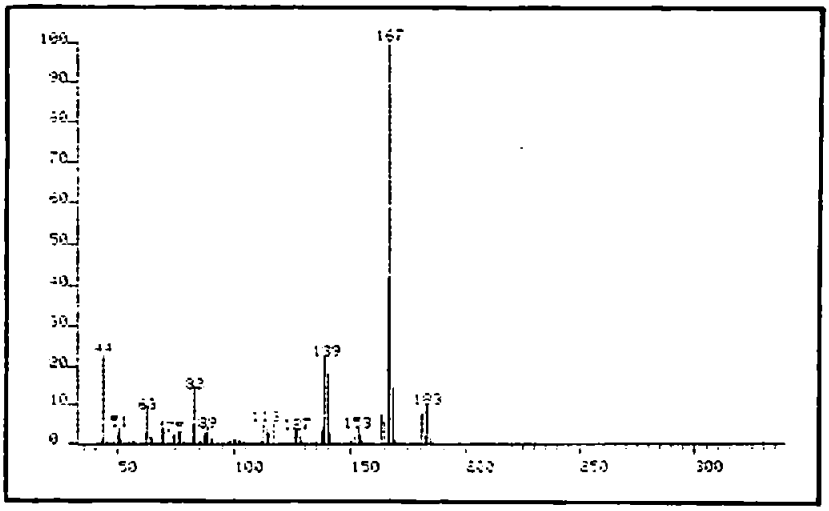


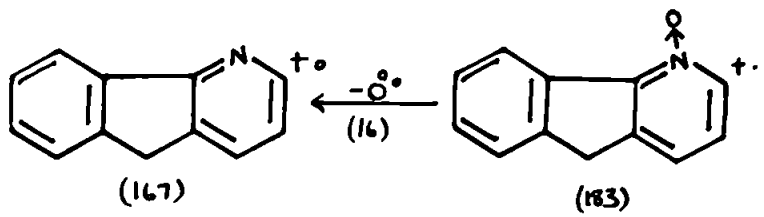


Appendix 1.61 5H-indeno[1,2-b]pyridine N-oxide (250)



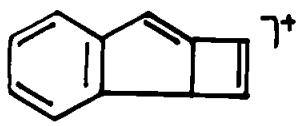
$C_{12}H_9NO$ RMM=183





(167) (183)

(28) -HCN -H·



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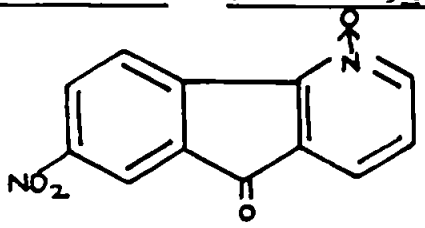
Appendix 1.62 7-nitro-5H-indeno[1,2-b]pyridin-5-one N-oxide (251)



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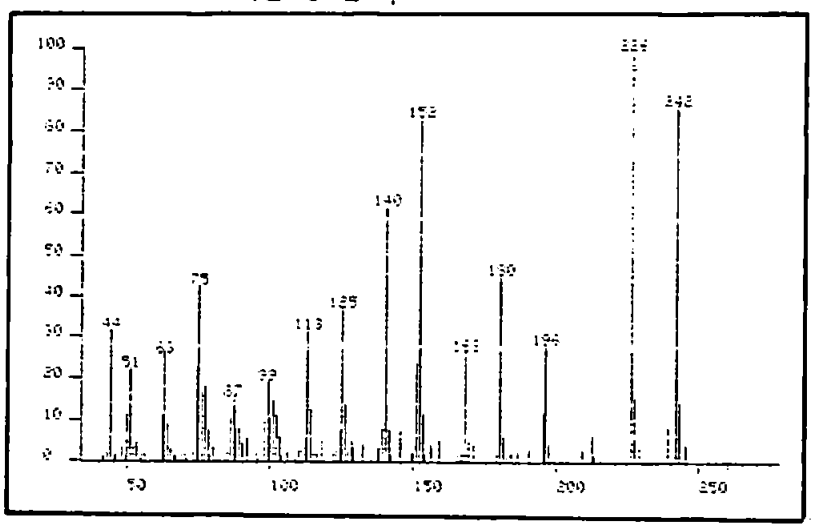
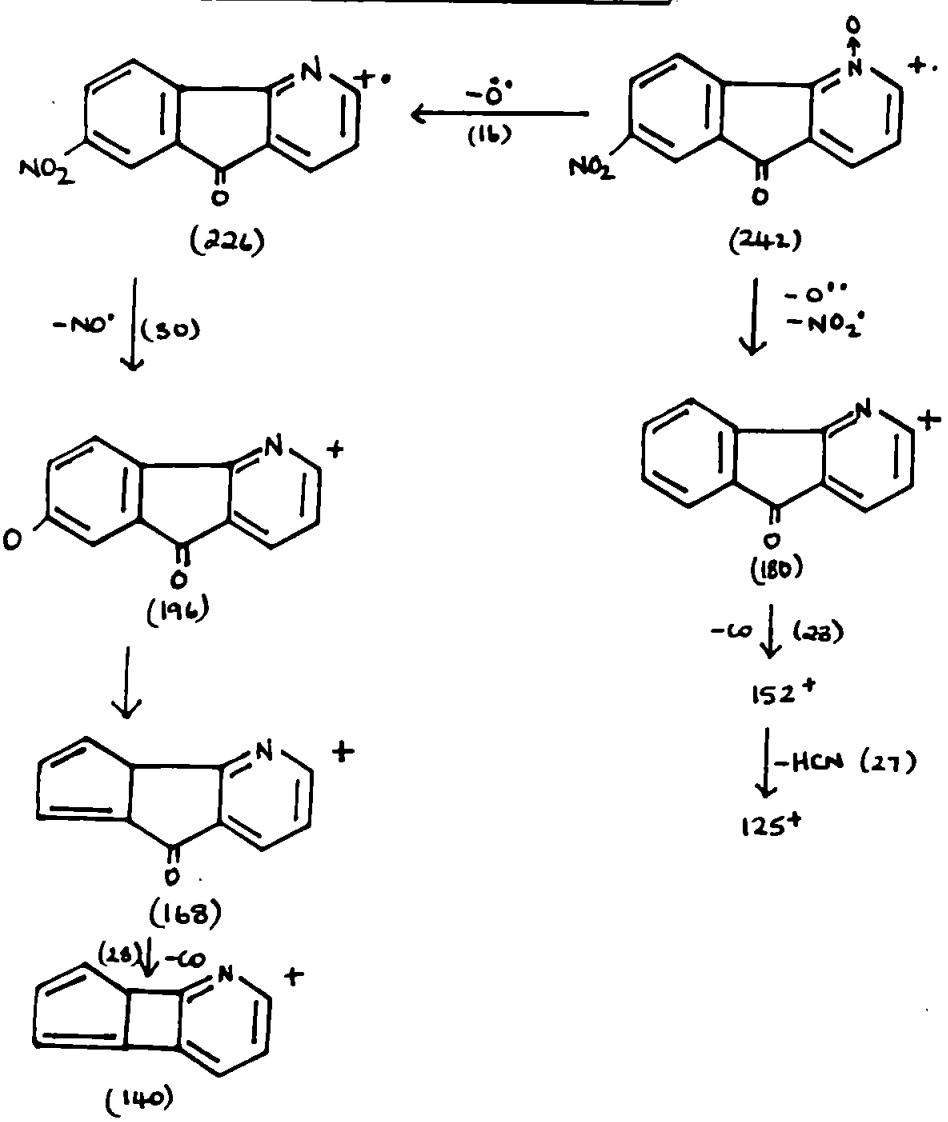
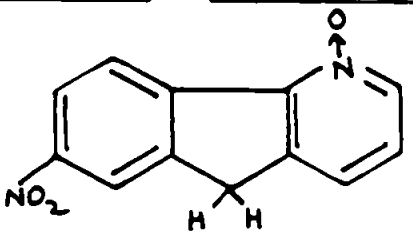
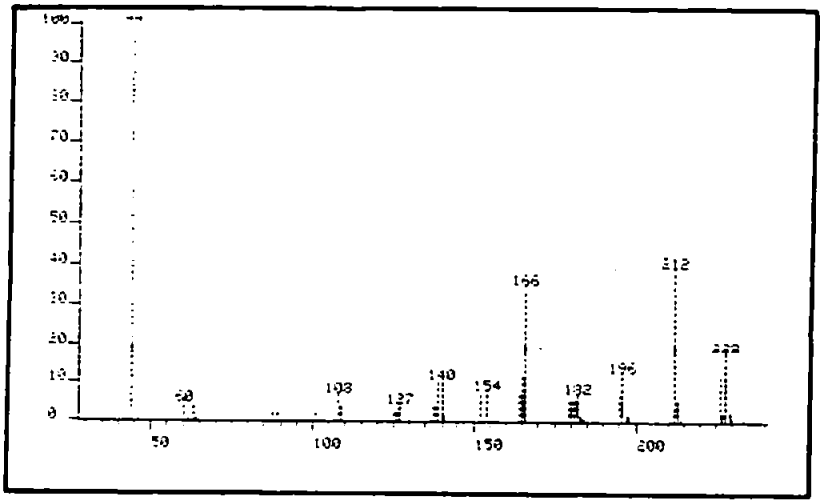


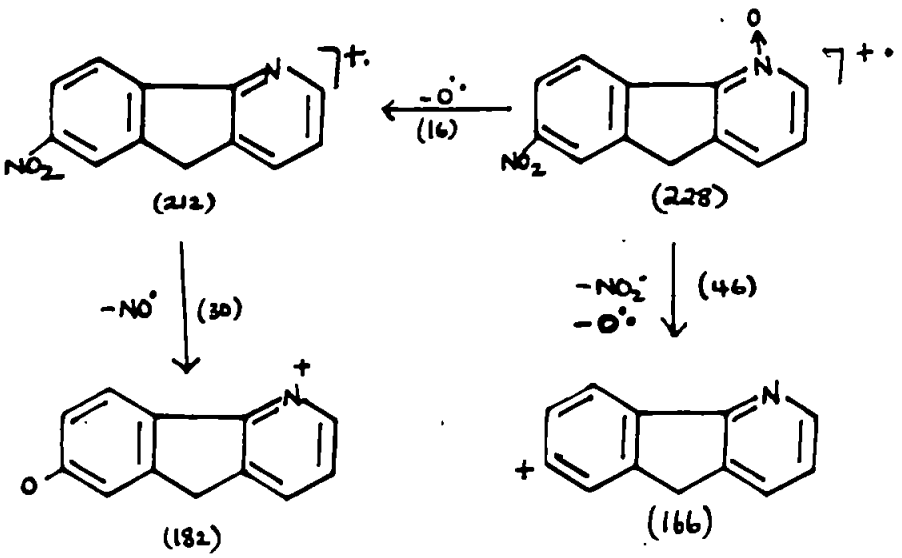


Appendix 1.63 7-nitro,5H-indeno [1,2-b] pyridine N-oxide (252)



$C_{12}H_8N_2O_3$ RMM=228





Appendix II

^{1}H NMR

Summary of ^{1}H NMR spectra (appendix II)

Formichov and co-workers[113] have undertaken a systematic analysis of the proton NMR spectra of three of the isomeric indenopyridines. In this study Formichov utilised suitably substituted fluorene compounds as models and carried out double resonance experiments linked with calculations of the theoretical spectra (using iterative procedures, ITRCAL) and was able to assign many of the resonances associated with these compounds.The assignments are summarised in Tables 5-8.

Table 5. Chemical Shifts of fluorenes and indenopyridines.

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	9-CH_2
1	---	8.25	7.11	7.93	7.67	7.20	7.17	7.42	3.85
2	8.70	----	8.48	7.70	7.81	7.31	7.37	7.58	4.10
4	7.74	7.09	8.38	----	7.89	7.31	7.28	7.46	3.58

Table 6. Coupling Constants, (J).

Compound	(12)	(13)	(14)	(23)	(24)	(34)	(56)	(57)	(58)
1	--	--	--	4.91	1.61	7.47	7.55	0.99	0.79
2	--	0	1.0	--	--	5.0	7.65	1.18	0.68
4	7.49	1.54	--	4.84	--	--	7.44	1.31	0.77

	(67)	(68)	(78)
1	7.58	1.07	7.51
2	7.49	1.06	7.58
3	7.12	0.99	7.37

Table 7. Long Range Coupling Constants (J).

Compound	(19)	(29)	(39)	(49)	(59)	(69)	(79)	(89)
1	–	0.25	-0.7	0.4	0.4	-0.7	0.25	-0.85
2	—	–	–	–	0.4	-0.7	0.25	-0.7
4	-0.85	0.25	-0.75	—	0.4	-0.7	0.25	-0.85

These studies show that the proton NMR spectrum of an indenopyridine compound can be treated as a simple superimposition of the $AMXY_2$ spectrum (pyridine protons) and a $ABCDX_2$ sub-spectrum (phenylene protons).The long range coupling (Table 8) can be identified in the single resonance spectrum with respect to the ^{13}C NMR assignments. These were deduced with reference to known ^{13}C shifts (δ) in model compounds (pyridine, quinoline and isoquinoline) and the effects of contact shift reagents; $Eu(dpm)_3$, $Pr(dpm)_3$ and $Gd(dpm)_3$.

Table 8. ^1H Chemical shifts, coupling constants and long range coupling constants of the 9-CH_2 protons with the aromatic protons of (1).

Assignment proton	δ ppm	Aromatic proton	J(Hz)	9-CH_2	J(Hz)
H-2	8.25	H-2,3	4.91	H-2,9	+0.3
H-3	7.11	H-2,4	1.61	H-3,9	-0.7
H-4	7.93	H-3,4	7.47	H-4,9	+0.4
H-5	7.67	H-5,6	7.79	H-5,9	+0.4
H-6	7.20	H-5,7	1.09	H-6,9	-0.7
H-7	7.17	H-5,8	0.81	H-7,9	+0.2
H-8	7.42	H-6,7	7.43	H-8,9	-0.7
		H-6,8	1.12		
		H-7,8	7.66		

The ^{1}H NMR spectra are recorded in Appendix II. The spectra obtained from the indenopyridine compounds prepared during this project all show comparable chemical shifts (δ), particularly for the protons in the pyridyl ring. Assignments have been made by comparison with those given for 5H-indeno[1,2-b]pyridine (4) by Formichov et al[113] (Table 5, page 283b).

The presence of substituents at the methylene position has little effect on the chemical shift of the proton adjacent to the pyridyl nitrogen (H-2) but can cause downfield shifts in the phenyl protons (H-6,7,8,9) and the protons (H-3,4) in the pyridyl ring.

The methylene protons are found at 3.751 - 3.875 ppm in the reference compound for this project, 5H-indeno [1,2-b] pyridine (4).This is slightly downfield from that given by Formichov et al[113], Table 5, 5-CH_2 3.58 ppm. The other reference proton used during proton assignment is H-2 which is found at 8.582 ppm for (4).This differs a little from that quoted by Formichov et al[113], 8.38 ppm.

For 2-phenyl-3-pyridine carboxylic acid (158) , appendix II.1 the proton of -COOH is so far downfield that it is not shown.

The quoted values of chemical shifts for the protons of (4) are also shown together with my values in appendix II.2 . Apart from 5-CH_2 and H-2 where there is a descepancy of 0.2ppm, the difference between found and quoted values are approximately 0.1 ppm.

The spectra for 5H-indeno[1,2-b] pyridin-5-one (8) shows that the methylene protons are missing.

Appendix II.4 shows the spectra for (RS)5-hydroxy-5H-indeno[1,2-b] pyridine (215). The methylene proton is shown 5.96 ppm, the hydroxyl proton is found at 5.55 ppm.

The NMR spectra of the hydrazone (55) shows the NH_2 protons upfield at 3.44 ppm, (Appendix II.5) ,the proton adjacent to the pyridyl nitrogen is also shifted slightly upfield at 8.2 ppm.

The fluorene protons of 9-hydroxy-9-propylfluorene (218) are found at the expected values (7.250 - 7.652 ppm), appendix II.7.The hydroxyl proton is found at 5.55 ppm, and the propyl group is found downfield at (2.1 - 0.7) ppm.

The hydroxyl proton of (222) has shifted upfield (6.53 ppm , appendix II.8) probably by the presence of the phenyl group.

The NMR spectra of various oximes are shown in appendices II.9,12,23 and 24. The protons of the oxime group are found downfield at 12.92 ppm for compound (4), 12,65 ppm for fluorenone oxime (II.12) and 13.145 ppm for the bromo-derivative (224).

The 5-acetamido derivative (230), the proton (5-H) adjacent to the substituent group is stongly deshielded (6.45 ppm) as is the proton adjacent to the pyridyl nitrogen (H-2), 9.25 ppm.The methyl protons are found, as expected, at δ = 2 ppm .[114]

Substitution of bromine in the C-7 position of (8) leads to a downfield shift in H-6 and H-8 ie adjacent protons. (Appendix II.14).In the dibromo derivative, protons adjacent to the bromine substituent are strongly deshielded, δ =8.6 ppm (H-6) and 8.12 (H-8),appendix II.15.

The spectra of the tetrabromo compound shows little difference from that of (4).The protons are shifted slightly downfield,but the methylene protons are in generally the same position (δ= 3.84 ppm),appendix II.16.

Appendix II.17 shows the NMR spectra of (238).The protons adjacent to the NO_2 group in the C-7 position are strongly deshielded (δ= 8.3 - 8.4 ppm).Reduction of (238) afforded 7-nitro-5H-indeno[1,2-b]pyridine (239) whose spectra is shown in appendix II.18.The methylene protons are found downfield at 4 ppm.The proton adjacent to the pyridyl nitrogen (H-2) is also deshielded (δ= 8.9 ppm).

Reduction of the nitro group afforded the amine (240), appendix II.19.The methylene protons are deshielded and found in the same position as the amine protons (δ=3.8 ppm). In the case of the oxo compound (8), the amine protons are strongly deshielded to 5.24 ppm.The proton adjacent to the pyridyl nitrogen (H-2) is also downfield at δ=10 ppm.

The hydroxyl proton of 7-hydroxy-5H-indeno[1,2-b]pyridin-5-one (242) is found , as expected[114], with standard values at δ = 3.54 ppm (appendix II.21).For the methylene compound, the hydroxyl proton is deshielded (δ = 6.89 ppm) as is H-2 (δ= 9.8 ppm), appendix II.22 .The methylene protons are shown ,as expected,[114] at δ =3.84 .

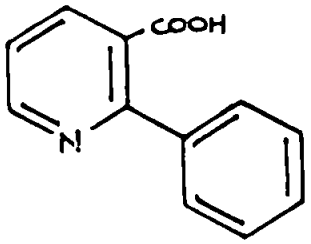
The structure of the diacetamido compound (246) is confirmed by NMR spectroscopy ,appendix II.25.The methyl protons are found at δ=1.9 ppm.The proton adjacent to the substituent group (H-5) is shielded (δ=3.443 ppm). H-2 is strongly deshielded at δ=10.3 ppm.

The presence of the N-oxide of (249),(250),(251) and (252) deshields the proton adjacent to the pyridyl nitrogen (H-2), δ= 8.6 ppm (appendix II.26) and δ=8.8 ppm (appendix II.28) for the oxo compounds (249 and 251 respectively).For the corresponding methylene compounds (250 and 252- appendix II.27 and II. 29 respectively) H-2 is more strongly deshielded , δ=8.8 ppm and δ=9.3 ppm respectively.The methylene protons are also deshielded at δ=3.97 and 4.10 ppm.

In general ^{1}H NMR was used to confirm that the correct structure had been assigned , ie the correct number of protons were present.Attempts have been made , by comparison with the reference compound (4) , to assign values to all the protons as shown in the following spectra (appendix II.1 - 29).

Appendix II.1

2-phenyl-3-pyridine carboxylic acid (158)



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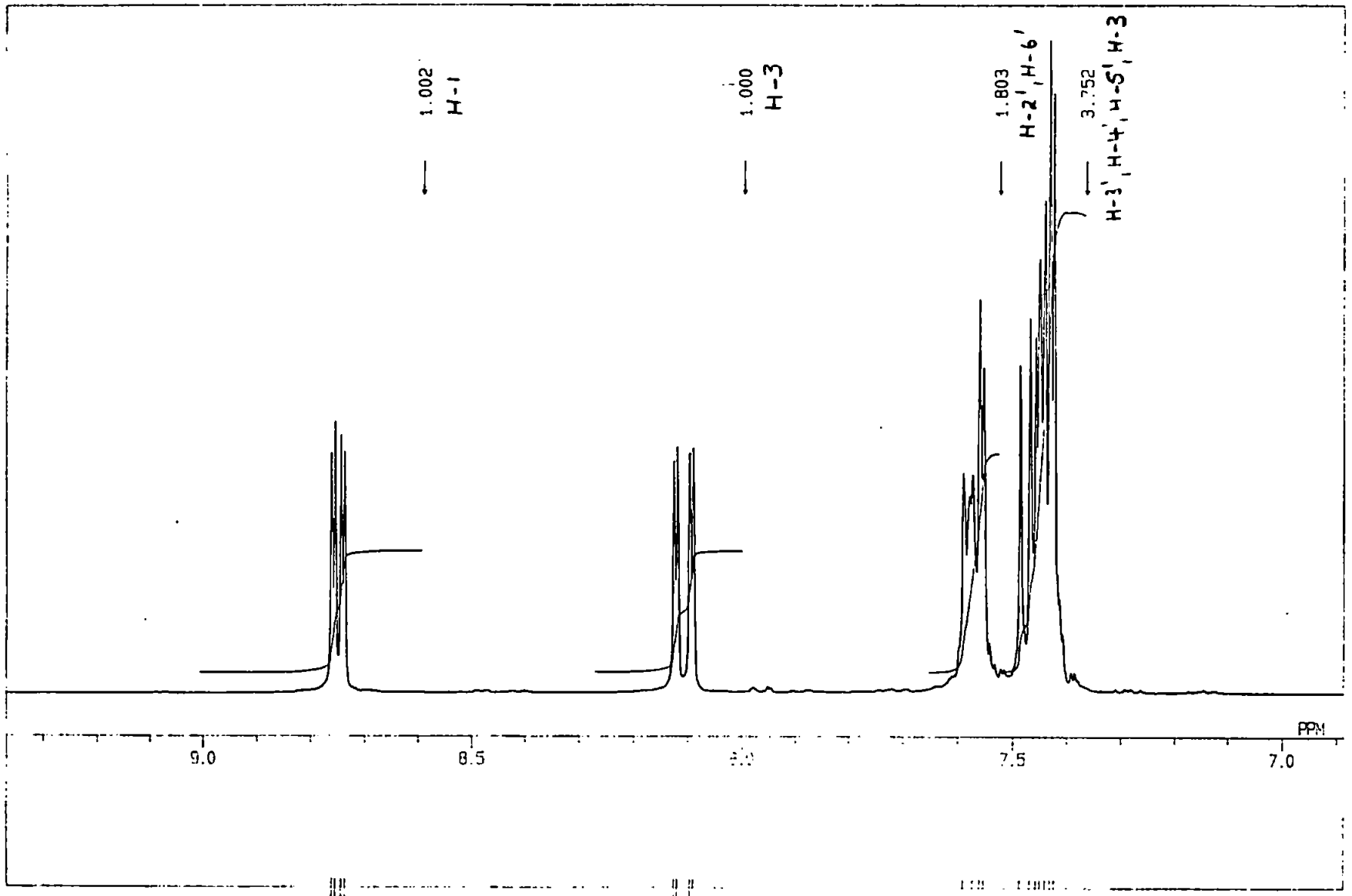
3		8.7439	39.48975	2362.30	5304	++++++++
4		8.7365	36.90810	2360.32	5310	+++++++
5	H-3	8.1259	35.50964	2195.36	5810	+++++++
6		8.1198	37.71547	2193.71	5815	++++++++
7		8.0966	36.73584	2187.44	5834	+++++++
8		8.0905	37.32411	2185.79	5839	++++++++
9	H2',6'	7.5898	33.77004	2050.52	6249	+++++++
10		7.5738	33.51010	2045.70	6263	+++++++
11		7.5605	60.38563	2042.60	6273	++++++++++++
12		7.5532	49.85262	2040.62	6279	++++++++++
13	H-3' H-4' H-5'	7.4860	50.31234	2022.48	6334	++++++++++
14		7.4677	57.46729	2017.53	6349	+++++++++++
15		7.4567	54.57528	2014.56	6358	+++++++++++
16		7.4494	66.49046	2012.58	6364	++++++++++++
17		7.4396	75.42451	2009.94	6372	+++++++++++++++
18	3	7.4311	100.00000	2007.63	6379	++++++++++++++++++++
19		7.4238	91.90796	2005.65	6385	++++++++++++++++++



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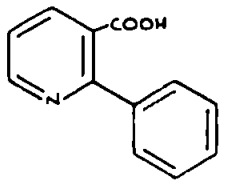
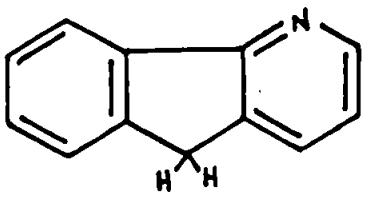


285

Appendix II.2

5H-indeno[1,2-b]pyridine (4)



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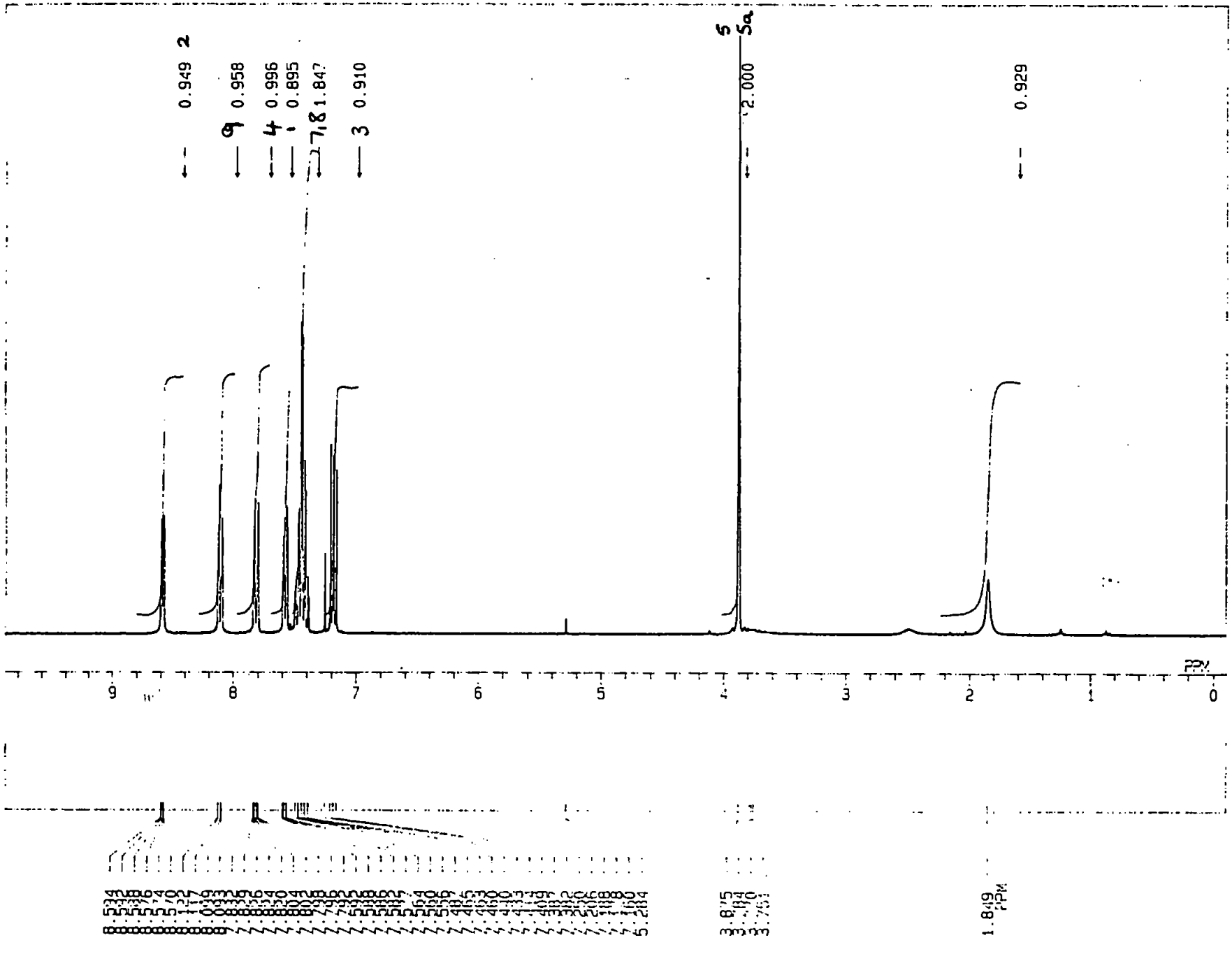
3		8.5884	17.59613	2320.30	5689	++++	8.38
4		8.5762	19.79631	2317.00	5699	++++	
5		8.5738	18.15279	2316.34	5701	++++	
6		8.5701	17.43697	2315.35	5704	+++	
7		8.1219	17.01816	2194.27	6071	+++	
8	H-9	8.1170	24.83040	2192.95	6075	+++++	
9		8.0987	12.75513	2188.00	6090	+++	7.89
10		8.0926	19.29855	2186.35	6095	++++	
11		7.8325	11.17469	2116.08	6308	++	
12		7.8288	18.32510	2115.09	6311	++++	
13		7.8264	18.66961	2114.43	6313	++++	
14		7.8240	20.50102	2113.77	6315	++++	
15	H-4	7.8203	9.89524	2112.78	6318	++	
16		7.8044	12.22007	2108.49	6331	++	7.70
17		7.8020	20.37851	2107.83	6333	++++	
18		7.7983	20.01845	2106.84	6336	++++	
19		7.7959	21.83139	2106.18	6338	++++	
20		7.7922	10.19686	2105.19	6341	++	
21		7.5919	13.29558	2051.08	6505	+++	
22		7.5883	15.10298	2050.09	6508	+++	
23		7.5858	16.29107	2049.43	6510	+++	
24	H-6	7.5822	10.62117	2048.44	6513	++	7.46
25		7.5773	5.31364	2047.12	6517	+	
26		7.5638	21.32133	2043.49	6528	++++	
27		7.5602	20.64668	2042.51	6531	++++	
28		7.5565	17.89456	2041.52	6534	++++	
29		7.4869	7.98253	2022.71	6591	++	
30		7.4649	19.73427	2016.77	6609	++++	
31		7.4625	19.04613	2016.11	6611	++++	
32	H-7	7.4600	20.64712	2015.45	6613	++++	
33		7.4405	52.26974	2010.17	6629	++++++++++	7.28 (7)
34	H-8	7.4332	49.77697	2008.19	6635	++++++++++	7.31 (8)
35		7.4136	28.95401	2002.91	6651	++++++	
36		7.4088	23.89390	2001.60	6655	+++++	
37		7.3868	9.52277	1995.66	6673	++	
38		7.3819	6.04157	1994.34	6677	+	
39		7.2500	13.48321	1958.71	6785	+++	
40		7.2060	31.71645	1946.83	6821	++++++	
41	H-3	7.1877	29.68678	1941.88	6836	++++++	7.09
42		7.1720	29.88632	1939.24	6844	++++++	
43		7.1596	27.36060	1934.29	6859	+++++	
44		5.2839	2.50897	1427.53	8395	+	
45		3.8747	100.00000	1046.81	9549	++++++++++++++++++++	
46	H-5	3.7843	5.32394	1022.39	9623	+	
47	H-5a	3.7697	8.31156	1018.43	9635	++	3.58
48		3.7513	8.19284	1013.49	9650	++	
49		1.8488	9.37990	499.47	11208	++	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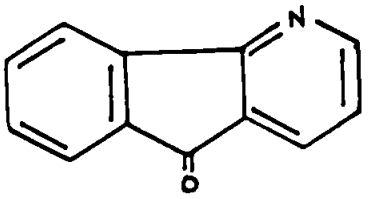
287

Appendix II.3

5H-indeno[1,2-b]pyridine-5-one (8).



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4		8.5445	41.25746	2308.45	5678	++++++++
5		7.8558	42.67570	2122.37	6242	+++++++++
6		7.8497	42.69756	2120.72	6247	+++++++++
7		7.8277	47.64318	2114.79	6265	++++++++++
8		7.8216	77.30376	2113.14	6270	+++++++++++++++
9		7.7935	48.33985	2105.55	6293	++++++++++
10		7.6848	40.47958	2076.19	6382	++++++++
11		7.6580	46.59201	2068.93	6404	+++++++++
12		7.5786	22.93501	2047.48	6469	+++++
13		7.5749	22.77874	2046.49	6472	+++++
14		7.5505	45.92699	2039.89	6492	+++++++++
15		7.5468	45.76140	2038.90	6495	+++++++++
16		7.5224	25.97321	2032.31	6515	+++++
17		7.5188	26.07643	2031.32	6518	+++++
18		7.4076	29.09429	2001.29	6609	++++++
19		7.4040	31.31809	2000.30	6612	++++++
20		7.3795	43.59440	1993.71	6632	+++++++++
21		7.3759	44.25306	1992.72	6635	+++++++++
22		7.3527	19.43796	1986.45	6654	++++
23		7.3490	19.77052	1985.46	6657	++++
24		7.1915	100.00000	1942.90	6786	++++++++++++++++++++
25		7.1768	46.40165	1938.94	6798	+++++++++
26		7.1585	42.92147	1933.99	6813	+++++++++
27		7.1487	41.51051	1931.35	6821	++++++++
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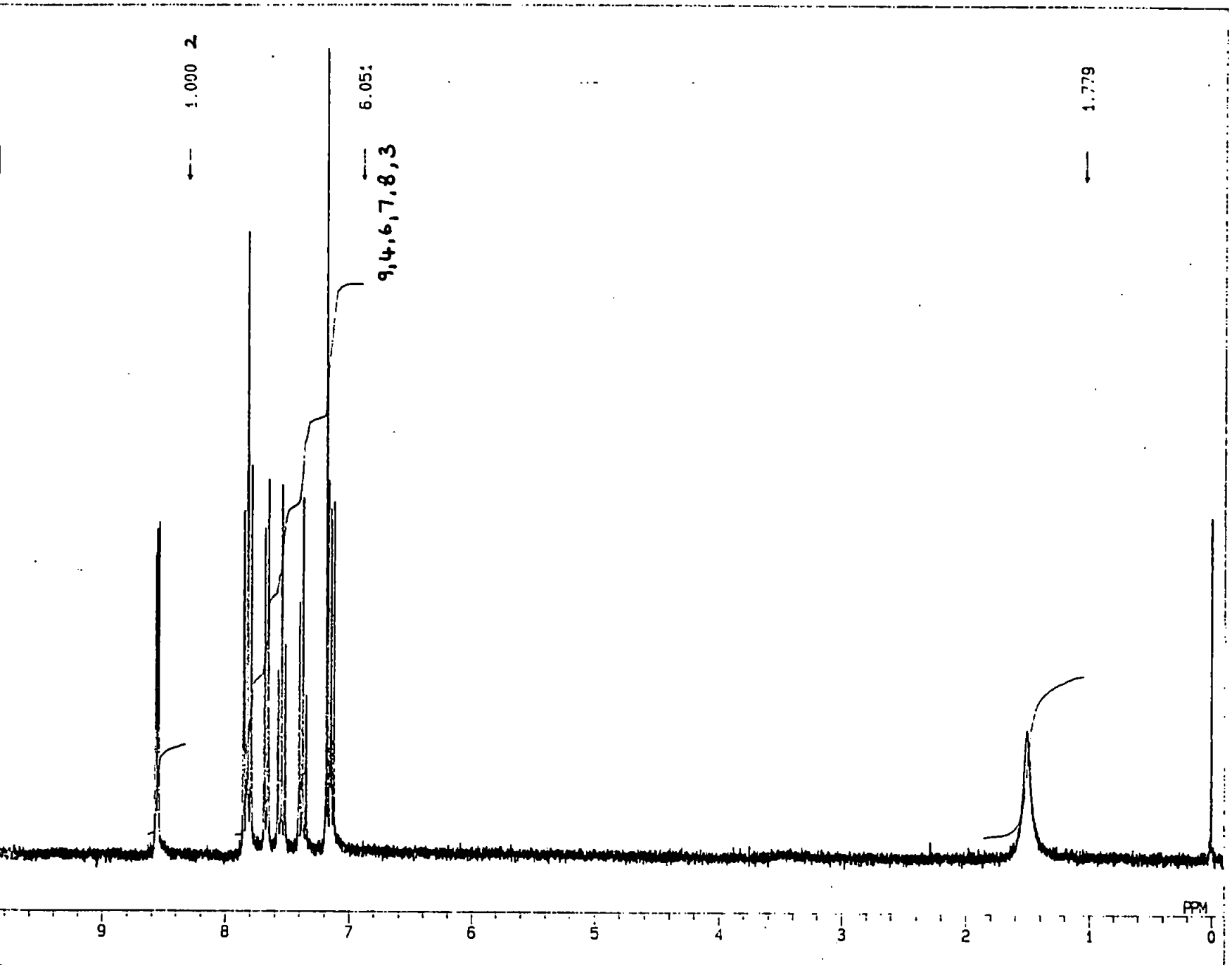
29		1.5033	15.84165	406.13	11444	+++



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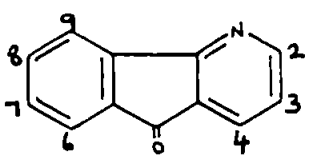
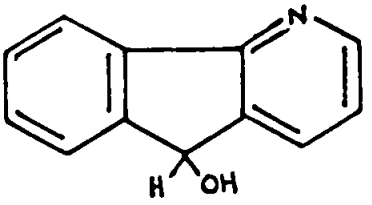


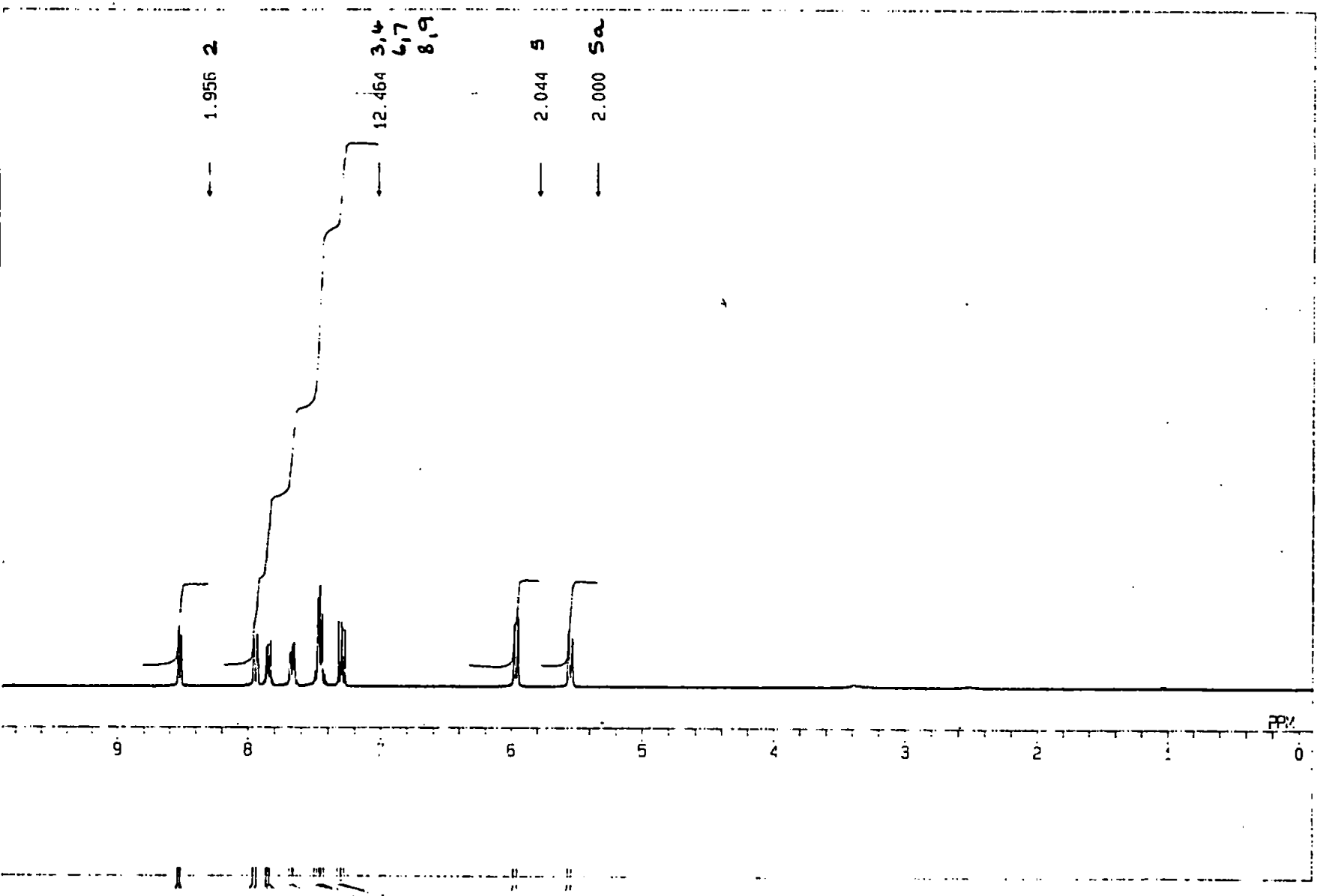
289

Appendix II.4

5-hydroxy,5H-indeno[1,2-b]pyridine (215)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H-2	8.5363	7.71719	2306.21	5476	++
2		8.5302	8.03855	2304.56	5481	++
3		8.5179	7.95898	2301.26	5491	++
4		8.5118	7.84478	2299.61	5496	++
5		7.9599	7.33127	2150.49	5948	+
6		7.9538	6.92039	2148.84	5953	+
7		7.9318	8.12983	2142.90	5971	++
8		7.9293	7.86410	2142.24	5973	++
9		7.8622	6.30176	2124.09	6028	+
10		7.8536	4.91029	2121.78	6035	+
11		7.8487	6.60983	2120.46	6039	+
12		7.8365	4.71307	2117.17	6049	+
13		7.8304	7.09952	2115.52	6054	+
14		7.6839	5.41635	2075.93	6174	+
15		7.6643	6.61500	2070.65	6190	+
16		7.6321	6.90864	2067.35	6200	+
17		7.4983	2.44849	2025.78	6326	
18		7.4763	13.83590	2019.84	6344	+++
19		7.4616	15.78874	2015.88	6356	+++
20		7.4519	8.36002	2013.24	6364	++
21		7.4457	11.33763	2011.59	6369	++
22		7.4250	1.83357	2005.98	6386	
23		7.3312	10.21554	1977.94	6471	++
24		7.3029	10.02958	1972.99	6486	++
25		7.2931	9.19118	1970.35	6494	++
26		7.2748	8.88646	1965.40	6509	++
27	5-OH	5.9779	9.78368	1615.03	7571	++
28		5.9510	10.88686	1607.77	7593	++
29	5-H	5.5627	8.54707	1502.85	7911	++
30		5.5358	7.53400	1495.60	7933	++



13-OCT-92 13:31:56

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	5.0 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

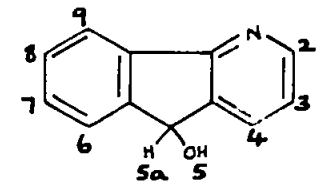
Processing

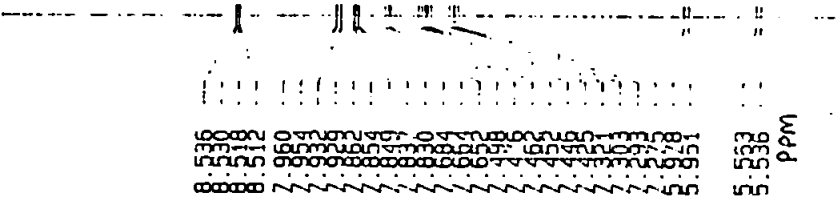
BF	0.10 Hz
EXREF	2.50 ppm

Plot

XS	86.3322 Hz
XE	2701.6640 Hz
YG	2.62

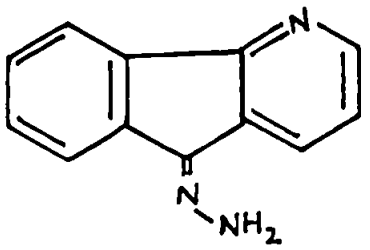
OPERATOR : _____



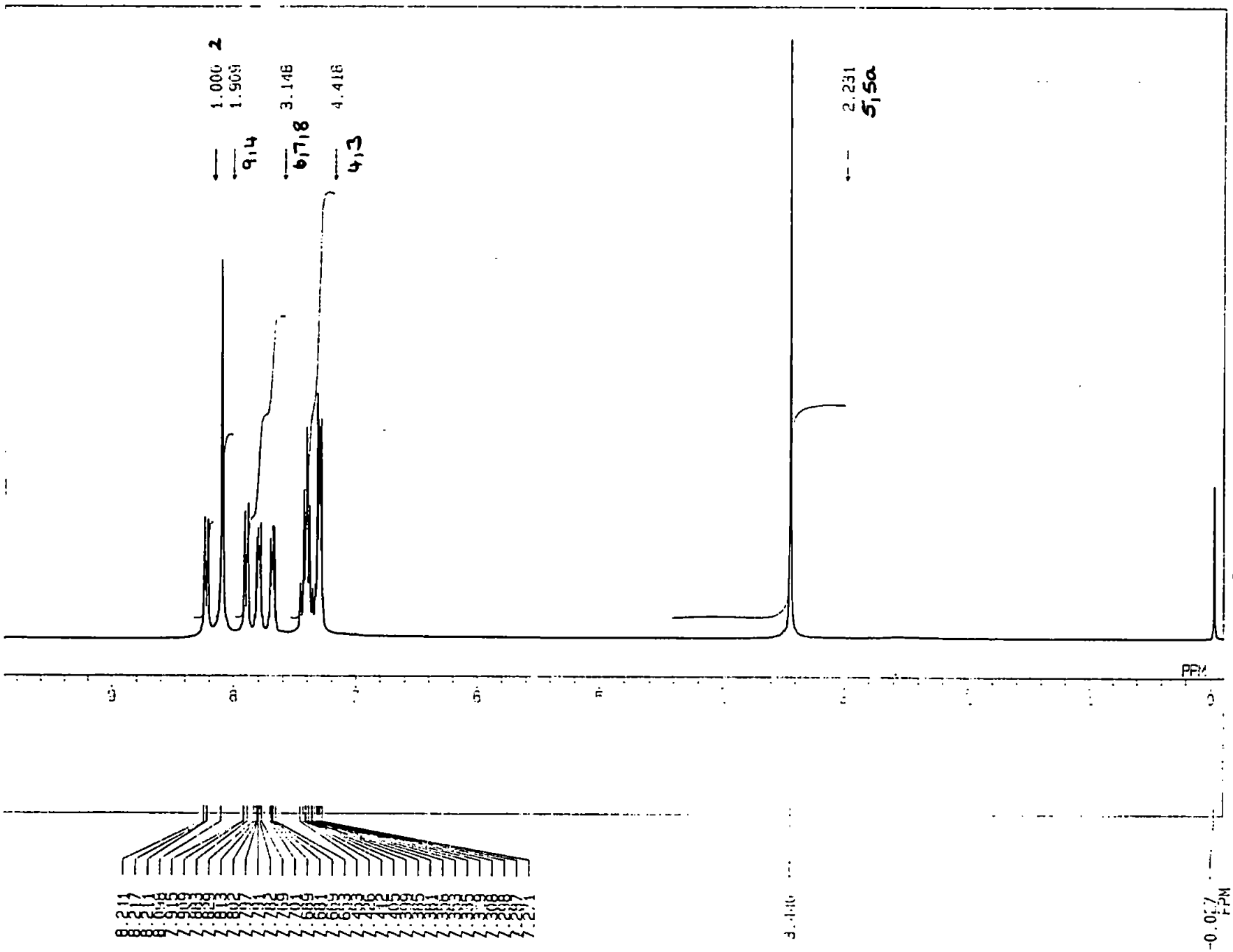


Appendix II.5

5H-indeno [1,2-b] pyridine-5-one hydrazone (**55**).



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.2407	20.13008	2226.37	5719	++++
2	H-2	8.2175	19.34641	2220.10	5738	++++
3		8.2114	19.71709	2218.45	5743	++++
4	H-9, H-4	8.0979	63.05788	2187.77	5836	++++++++++++
5		7.9147	17.57796	2138.26	5986	++++
6		7.9086	21.14243	2136.63	5991	++++
7		7.8829	22.43598	2129.70	6012	++++
8	H-6	7.8292	3.68283	2115.19	6056	+
9	H-7'	7.8133	16.73531	2110.90	6069	+++
10		7.8023	18.31577	2107.93	6078	++++
11	H-8	7.7974	14.42209	2106.61	6082	+++
12		7.7913	15.08119	2104.96	6087	+++
13		7.7816	19.06857	2102.32	6095	++++
14		7.7694	3.72718	2099.02	6105	+
15		7.7010	16.55059	2080.54	6161	+++
16		7.6888	14.25462	2077.25	6171	+++
17		7.6814	18.64594	2075.27	6177	++++
18		7.6692	18.51789	2071.97	6187	++++
19		7.6533	4.21000	2067.68	6200	+
20		7.4531	8.99682	2013.57	6364	++
21		7.4262	24.60558	2006.31	6386	+++++
22		7.4116	20.89749	2002.35	6398	++++
23		7.4054	35.06179	2000.70	6403	+++++++
24		7.3993	25.54593	1999.05	6408	+++++
25		7.3847	20.16868	1995.10	6420	++++
26		7.3810	21.93483	1994.11	6423	++++
27	H-4	7.3578	8.18749	1987.84	6442	++
28		7.3529	7.84036	1986.52	6446	++
29	H-3	7.3346	8.88429	1981.57	6461	++
30		7.3187	40.83220	1977.28	6474	++++++++
31		7.3078	36.24289	1974.31	6483	+++++++
32		7.2980	35.10900	1971.67	6491	+++++++
33		7.2870	36.47753	1968.70	6500	+++++++
34		7.2711	6.87946	1964.41	6513	+
35	H5,5a -	3.4403	100.00000	929.45	9650	++++++++++++++++++++



26-NOV-92 14:40:21

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

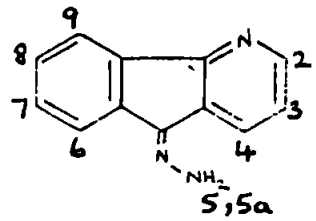
Processing

BF	0.10 Hz
EXREF	2.50 ppm

Plot

XS	86.6620 Hz
XE	2701.6640 Hz
YG	2.26

OPERATOR : _____



5,5a

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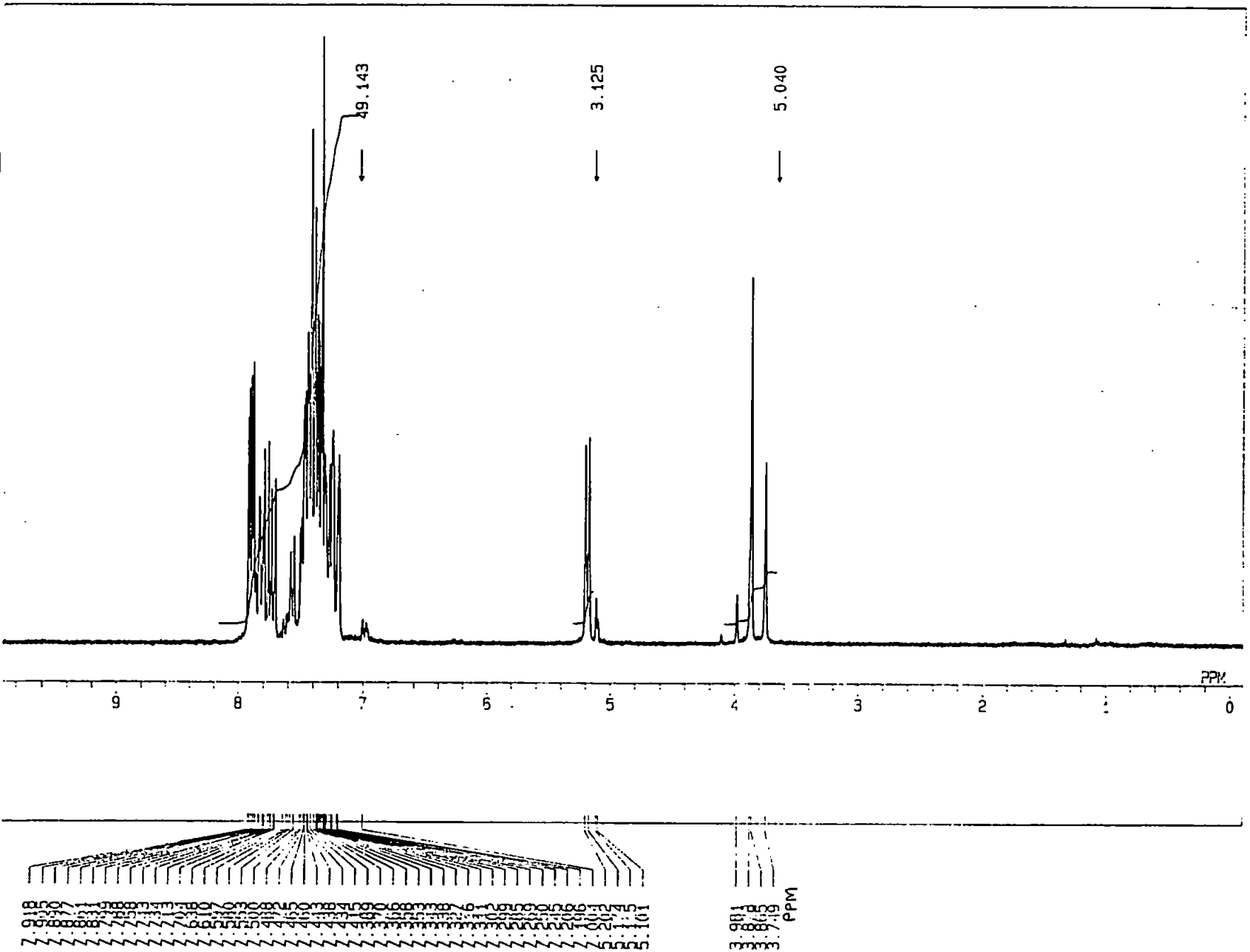
Appendix II.6

9,9'-bifluorenyl (217).

0.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	7.9180	37.15395	2139.17	6301	+++++++
2	7.9045	42.03420	2135.54	6312	++++++++
3	7.8899	44.00806	2131.58	6324	+++++++++
4	7.8765	46.28682	2127.95	6335	+++++++++
5	7.8606	11.44968	2123.67	6348	++
6	7.8313	23.99551	2115.75	6372	+++++
7	7.7995	21.22857	2107.17	6398	++++
8	7.7885	31.95950	2104.20	6407	++++++
9	7.7580	33.24272	2095.95	6432	+++++++
10	7.7434	9.89065	2091.99	6444	++
11	7.7336	25.34145	2089.35	6452	+++++
12	7.7128	10.27827	2083.75	6469	++
13	7.7043	27.01145	2081.44	6476	+++++
14	7.6383	3.68588	2063.62	6530	+
15	7.6102	4.53868	2056.03	6553	+
16	7.5968	4.75723	2052.40	6564	+
17	7.5797	14.89922	2047.78	6578	+++
18	7.5529	17.53671	2040.53	6600	++++
19	7.5003	18.88774	2026.34	6643	++++
20	7.4881	20.57519	2023.04	6653	++++
21	7.4723	29.26815	2018.75	6666	+++++++
22	7.4649	40.13394	2016.77	6672	+++++++
23	7.4603	41.59255	2015.45	6676	+++++++
24	7.4429	51.26921	2010.83	6690	++++++++++
25	7.4381	48.01890	2009.51	6694	++++++++++
26	7.4344	43.11633	2008.52	6697	+++++++++
27	7.4149	84.84431	2003.24	6713	+++++++++++++++++
28	7.3892	71.88445	1996.32	6734	++++++++++++
29	7.3697	53.41574	1991.04	6750	++++++++++
30	7.3660	54.14349	1990.05	6753	++++++++++
31	7.3575	53.08626	1987.74	6760	++++++++++
32	7.3523	48.98534	1986.42	6764	++++++++++
33	7.3428	49.17454	1983.78	6772	++++++++++
34	7.3379	52.70433	1982.46	6776	++++++++++
35	7.3269	100.00000	1979.49	6785	++++++++++++++++++++
36	7.3159	24.09081	1976.52	6794	+++++
37	7.3111	31.12266	1975.20	6798	++++++
38	7.3025	27.51127	1972.89	6805	++++++
39	7.2988	26.52003	1971.90	6808	+++++
40	7.2854	12.39554	1968.27	6819	++
41	7.2695	29.43964	1963.98	6832	++++++
42	7.2500	33.25855	1958.71	6848	+++++++
43	7.2451	35.08886	1957.39	6852	+++++++
44	7.2060	25.56084	1946.83	6884	+++++
45	7.1963	31.02998	1944.19	6892	++++++
46	7.0045	3.70742	1892.39	7049	+
47	5.2031	32.85504	1405.43	8525	+++++++
48	5.1740	34.04681	1397.84	8548	+++++++
49	5.1154	7.41002	1382.01	8596	+
50	5.1007	3.88665	1378.05	8608	+
51	3.9809	8.04998	1075.51	9525	++
52	3.8783	15.51826	1047.80	9609	+++
53	3.8649	60.50812	1044.17	9620	++++++++++
54	3.7429	30.07630	1012.83	9715	++++++



09-MAR-93 11:37:20

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

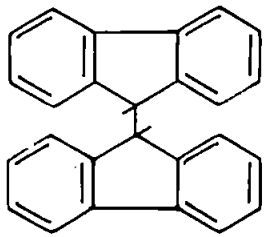
Processing

BF	0.10 Hz
EXREF	7.25 ppm

Plot

XS	191.4786 Hz
XE	2701.6630 Hz
YG	2.09

OPERATOR : _____



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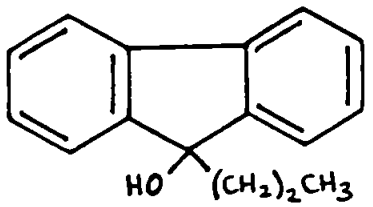
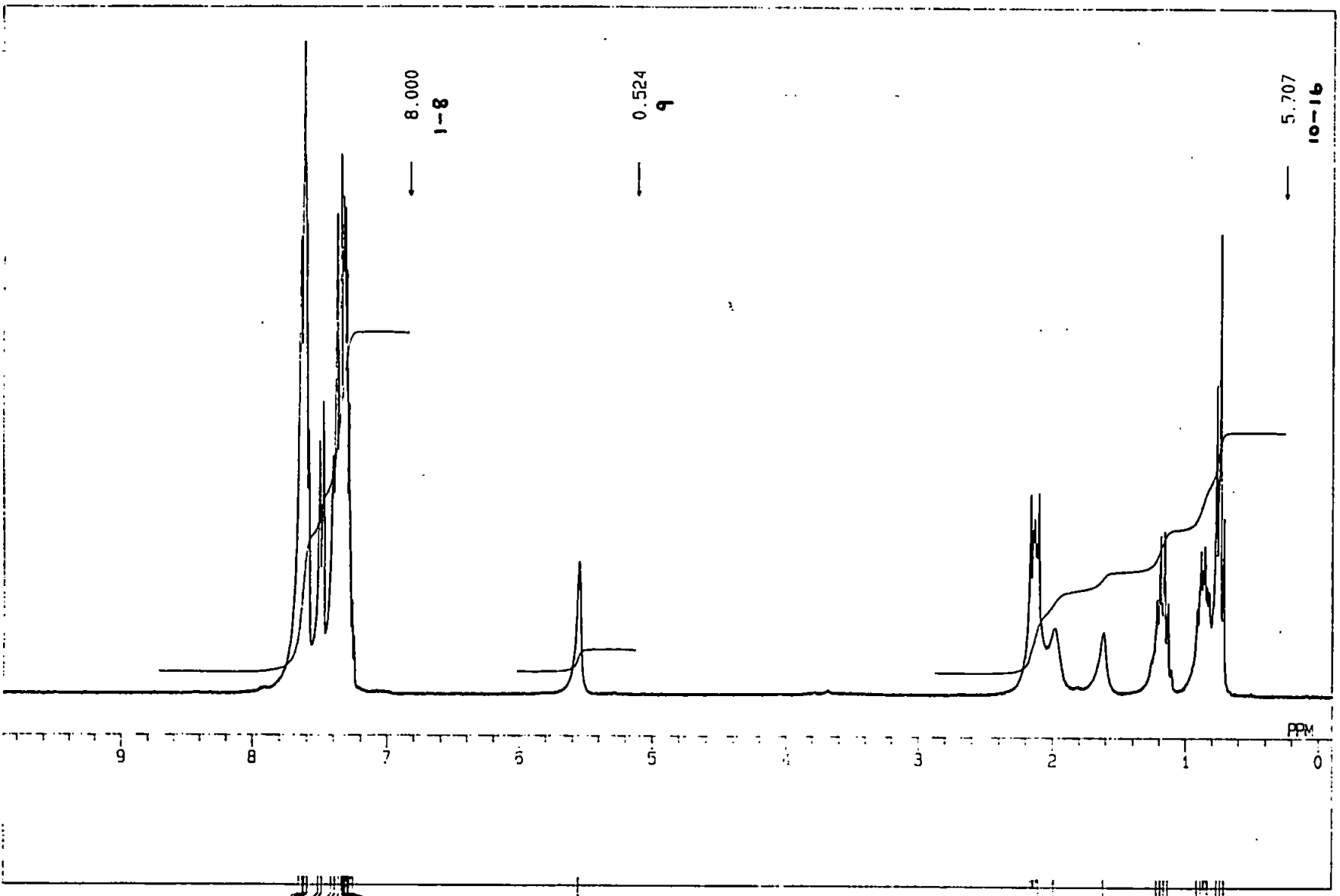
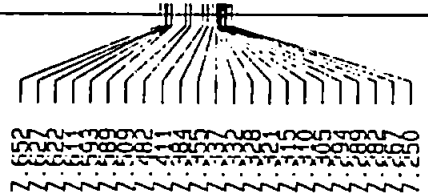
Appendix II.7

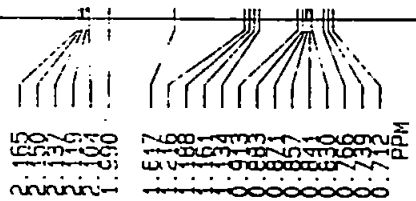
9-hydroxy,9-propyl-fluorene (218)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		7.6518	70.19701	2067.25	6458	+++++++++++++
2		7.6273	100.00000	2060.65	6478	++++++++++++++++++++
3		7.6225	82.43183	2059.33	6482	+++++++++++++++++
4		7.6115	72.07454	2056.36	6491	+++++++++++++
5		7.5931	40.41816	2051.41	6506	++++++++
6		7.5895	38.25848	2050.42	6509	++++++++
7		7.5089	38.71881	2028.65	6575	++++++++
8		7.4820	44.82117	2021.39	6597	+++++++++
9		7.4112	36.43407	2002.26	6655	+++++++
10	1-4,	7.3843	73.70530	1995.00	6677	++++++++++++++
11	6-9	7.3550	82.84719	1987.08	6701	+++++++++++++++++
12		7.3367	76.23461	1982.13	6716	++++++++++++++
13		7.3318	75.72600	1980.81	6720	++++++++++++++
14		7.3282	68.50676	1979.82	6723	++++++++++++++
15		7.3208	74.55138	1977.84	6729	++++++++++++++
16		7.3147	64.86766	1976.19	6734	++++++++++++
17		7.3098	64.41399	1974.87	6738	++++++++++++
18		7.3050	49.70388	1973.55	6742	++++++++++
19		7.2940	44.43909	1970.58	6751	+++++++++
20		7.2891	33.89579	1969.26	6755	+++++++
21		7.2818	21.78992	1967.28	6761	++++
22		7.2671	14.15777	1963.32	6773	+++
23		7.2500	8.68945	1958.71	6787	++
24	9 –	5.5501	20.33730	1499.46	8179	++++
25		2.1650	30.91479	584.92	10951	++++++
26		2.1504	25.43774	580.96	10963	+++++
27		2.1369	27.08398	577.33	10974	+++++
28		2.1186	23.35378	572.38	10989	+++++
29	CH_2	2.1040	31.13761	568.42	11001	++++++
30		1.9904	10.40569	537.74	11094	++
31	CH_2	1.6167	9.86595	436.79	11400	++
32		1.2162	14.82455	328.57	11728	+++
33	CH_3	1.1881	24.60990	320.98	11751	+++++
34		1.1612	25.21171	313.73	11773	+++++
35		1.1344	14.26538	306.47	11795	+++
36		0.9133	13.40392	246.75	11976	+++
37		0.8828	22.23719	238.50	12001	++++
38		0.8706	19.30473	235.20	12011	++++
39		0.8572	23.02217	231.58	12022	+++++
40		0.8413	16.68278	227.29	12035	+++
41		0.8303	16.04228	224.32	12044	+++
42		0.7656	47.72605	206.83	12097	++++++++++
43		0.7387	70.94933	199.57	12119	++++++++++++
44		0.7118	27.23301	192.32	12141	+++++







21-APR-93 11:22:45

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

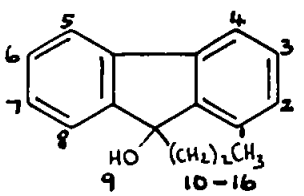
Processing

BF	0.10 Hz
EXREF	7.25 ppm

Plot

XS	171.3534 Hz
XE	2701.6630 Hz
YG	3.63

OPERATOR : _____



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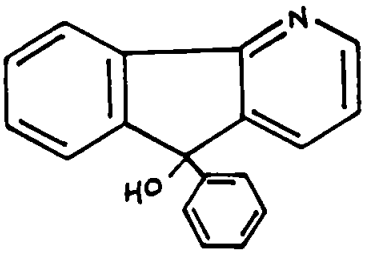
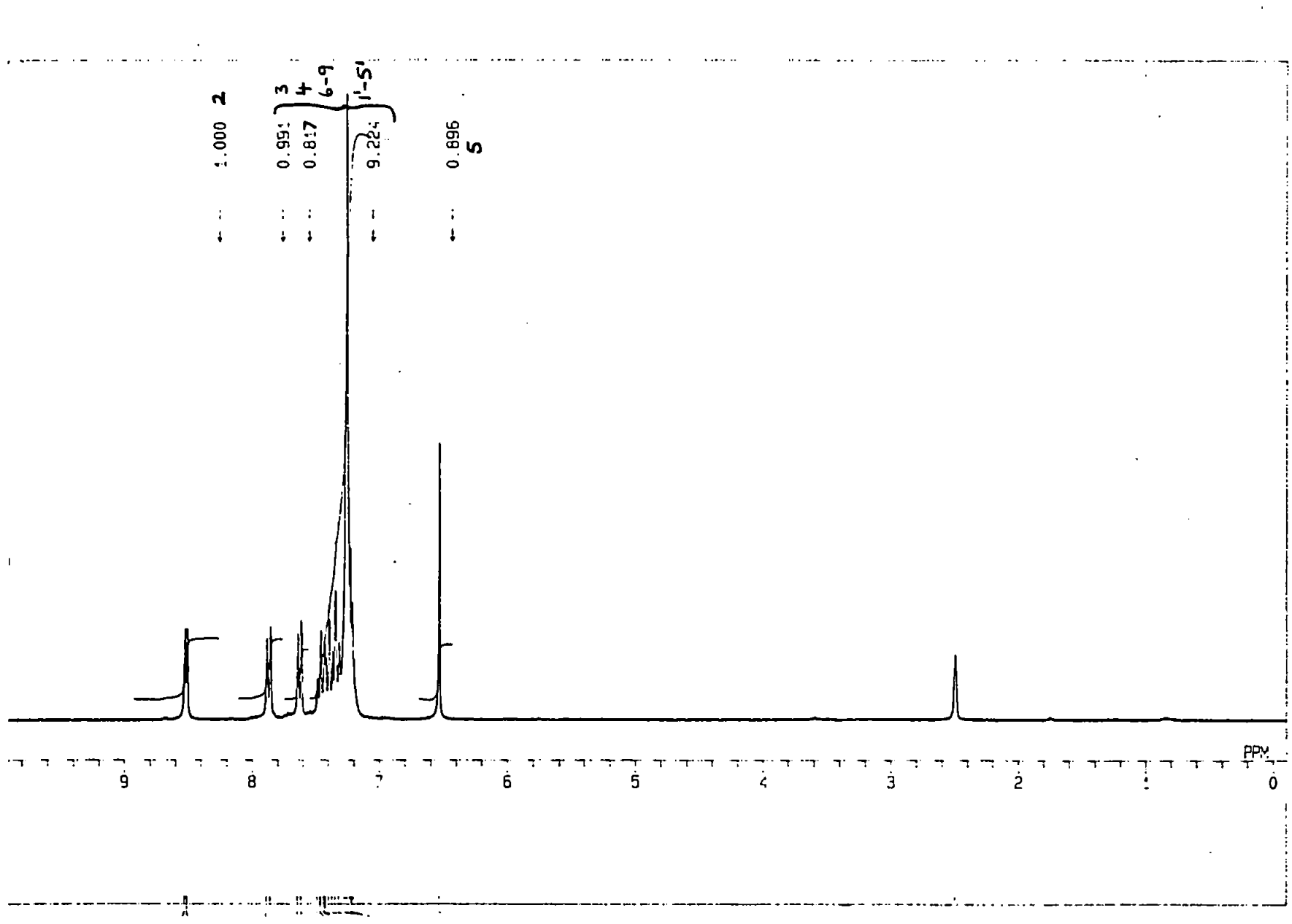
Appendix II.8

5-hydroxyl-5-phenylindeno[1,2-b]pyridine (222)



		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.5289	14.25649	2304.23	5482	+++
2	H-2	8.5240	14.45491	2302.91	5486	+++
3		8.5106	14.56941	2299.28	5497	+++
4		8.5057	13.27057	2297.96	5501	+++
5		7.8842	12.95056	2130.03	6010	+++
6		7.8585	14.82528	2123.10	6031	+++
7		7.6448	13.76741	2065.37	6206	+++
8		7.6387	13.05415	2063.72	6211	+++
9		7.6187	15.80653	2057.78	6229	+++
10		7.6113	13.91302	2056.46	6233	+++
11		7.4843	6.51377	2022.15	6337	+
12		7.4628	14.10253	2016.21	6355	+++
13		7.4580	14.09193	2014.89	6359	+++
14		7.4360	11.39049	2008.95	6377	++
15		7.4299	11.94343	2007.30	6382	++
16		7.4238	9.83994	2005.65	6387	++
17		7.4177	9.59650	2004.00	6392	++
18		7.3957	15.97981	1998.06	6410	+++
19		7.3688	10.94358	1990.81	6432	++
20		7.3456	20.68281	1984.54	6451	++++
21		7.3187	12.26701	1977.28	6473	++
22		7.2711	45.41725	1964.41	6512	+++++++++
23		7.2540	100.00000	1959.79	6526	++++++++++++++++++++
24		7.2320	27.40658	1953.86	6544	+++++
25		7.2211	18.55423	1950.89	6553	++++
26		7.2137	18.65976	1948.91	6559	++++
27		7.2027	9.53578	1945.94	6568	++
28	5-OH -	6.5348	44.20272	1765.47	7115	+++++++++



16-OCT-92 14:35:02

Accumulation

OBS LC 1H
OFR 270.05 MHz
EXMOD LC1
POINT 32768
PW1 5.0 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SOLVENT DMSO

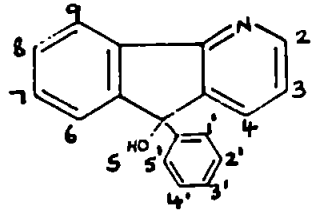
Processing

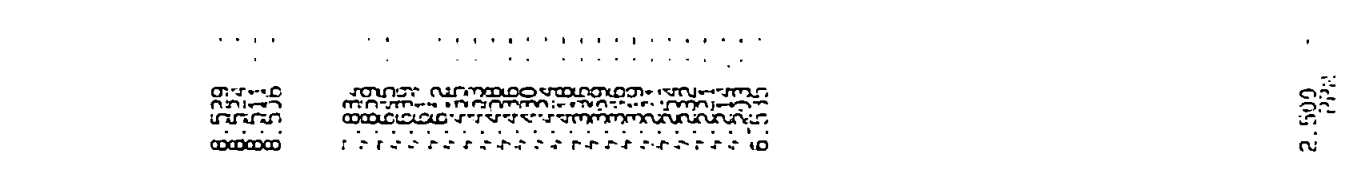
BF 0.10 Hz
EXREF 2.50 ppm

Plot

XS 86.3322 Hz
XE 2701.6640 Hz
YG 2.90

OPERATOR : _____





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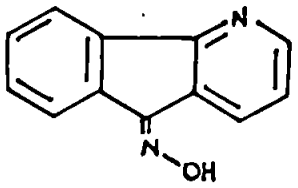
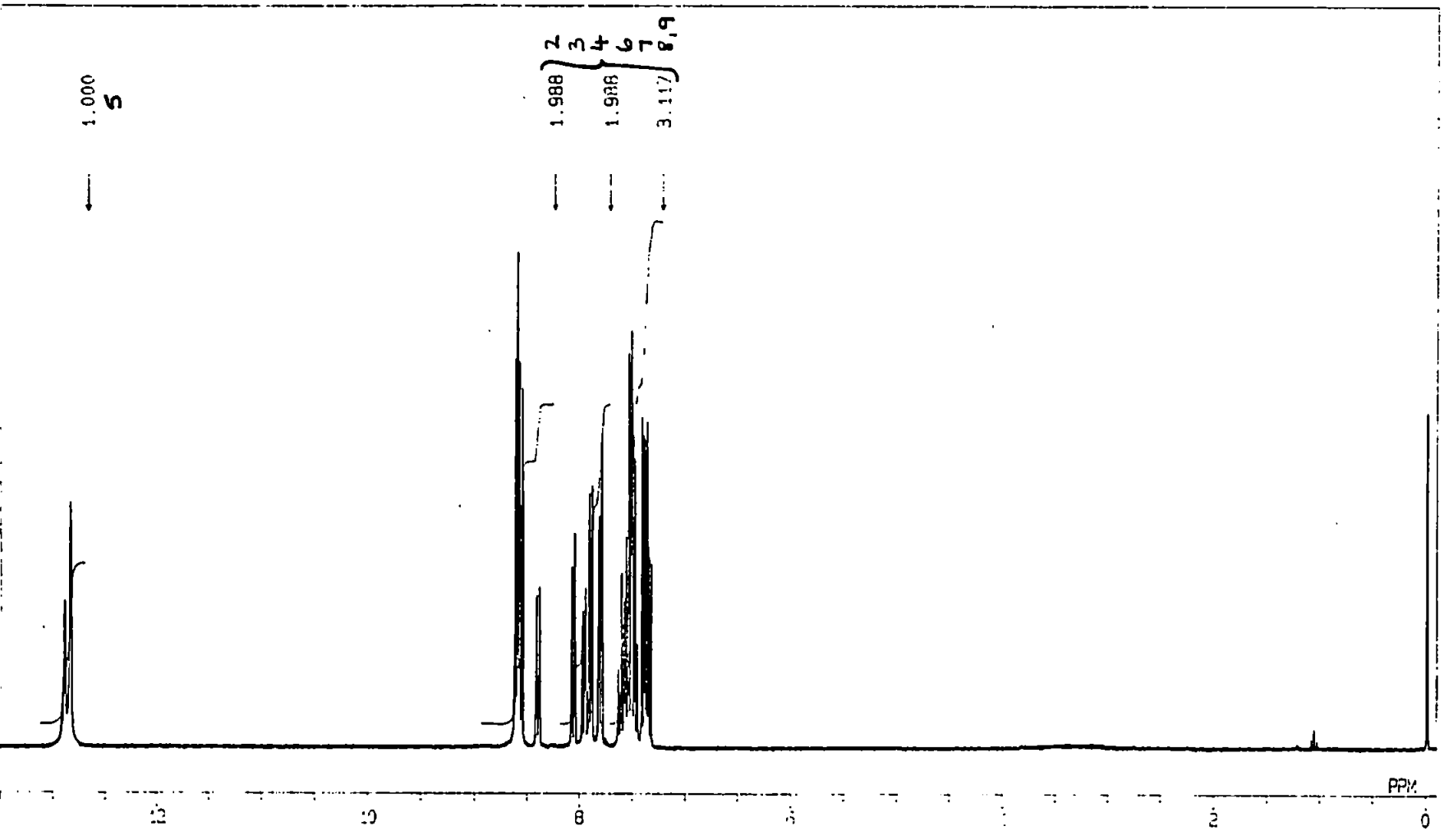
Appendix II.9

5H-indeno[1,2-b]pyridine-5-one oxime (224)



NO.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	8.6181	40.54752	2328.31	5407	++++++++
2	8.6120	55.21707	2326.66	5412	++++++++++
3	8.5998	43.73127	2323.37	5422	+++++++++
4	8.5924	70.33833	2321.39	5428	+++++++++++++
5	8.5863	32.88206	2319.74	5433	+++++++
6	8.5778	54.74132	2317.43	5440	++++++++++
7	8.5717	54.50809	2315.78	5445	++++++++++
8	8.5680	34.24039	2314.79	5448	+++++++
9	8.5485	51.05750	2309.51	5464	++++++++++
10	8.5436	38.77770	2308.19	5468	++++++++
11	8.4093	21.55625	2271.90	5578	++++
12	8.4056	15.24718	2270.91	5581	+++
13	8.3848	22.87714	2265.30	5598	+++++
14	8.0734	25.64328	2181.17	5853	+++++
15	8.0685	25.16087	2179.85	5857	+++++
16	8.0453	30.47155	2173.58	5876	++++++
17	8.0392	25.87811	2171.92	5881	+++++
18	7.9696	17.33361	2153.13	5938	++++
19	7.9660	19.45123	2152.14	5941	++++
20	7.9452	16.99874	2146.53	5958	+++
21	7.9403	22.64487	2145.21	5962	+++++
22	7.9098	29.39225	2136.96	5987	++++++
23	7.9049	36.08738	2135.64	5991	+++++++
24	7.8866	25.59503	2130.69	6006	+++++
25	7.8817	37.21064	2129.37	6010	+++++++
26	7.8133	32.96597	2110.90	6066	+++++++
27	7.8084	21.60796	2109.58	6070	++++
28	7.7901	43.30707	2104.63	6085	+++++++++
29	7.7865	32.57656	2103.64	6088	+++++++
30	7.6338	9.71577	2062.40	6213	++
31	7.6289	11.10954	2061.08	6217	++
32	7.6057	23.99999	2054.81	6236	+++++
33	7.6021	24.87748	2053.82	6239	+++++
34	7.5801	20.92046	2047.88	6257	++++
35	7.5740	19.64758	2046.23	6262	++++
36	7.5630	24.73349	2043.26	6271	+++++
37	7.5581	30.00395	2041.94	6275	++++++
38	7.5349	56.08389	2035.68	6294	++++++++++
39	7.5300	53.54050	2034.36	6298	++++++++++
40	7.5080	59.16579	2028.42	6316	+++++++++++
41	7.5007	50.25648	2026.44	6322	++++++++++
42	7.4787	41.09349	2020.50	6340	++++++++
43	7.4738	34.91635	2019.18	6344	+++++++
44	7.4519	14.79902	2013.24	6362	+++
45	7.4470	11.38694	2011.92	6366	++
46	7.4067	46.99895	2001.03	6399	+++++++++
47	7.3871	44.24201	1995.75	6415	+++++++++
48	7.3774	43.76059	1993.12	6423	+++++++++
49	7.3652	32.30122	1989.82	6433	++++++
50	7.3590	46.41885	1988.17	6438	+++++++++
51	7.3468	28.49280	1984.87	6448	++++++
52	7.3371	26.91062	1982.23	6456	+++++
53	7.3137	26.09123	1977.28	6471	+++++



07-DEC-92 09: 33: 24

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

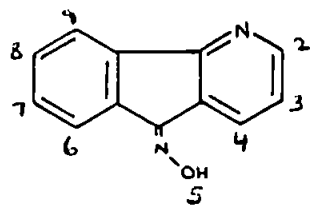
Processing

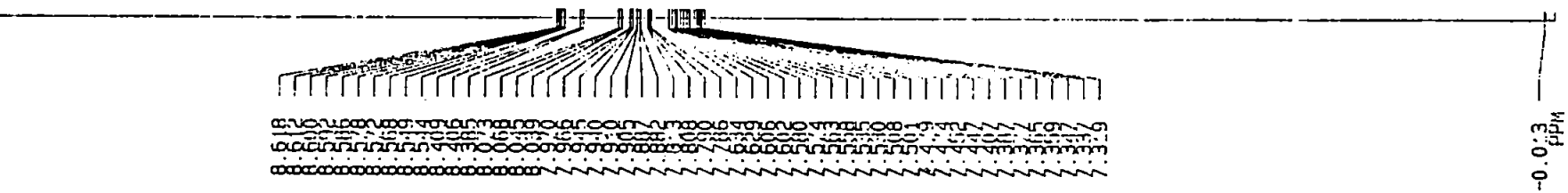
BF	0.10 Hz
EXREF	2.50 ppm

Plot

XS	-400.6273 Hz
XE	3674.2630 Hz
YG	2.94

OPERATOR : _____





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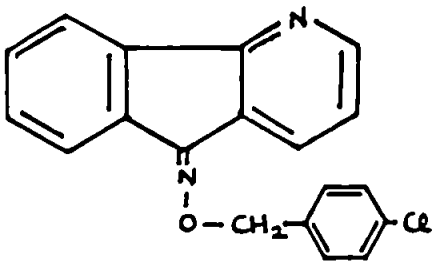
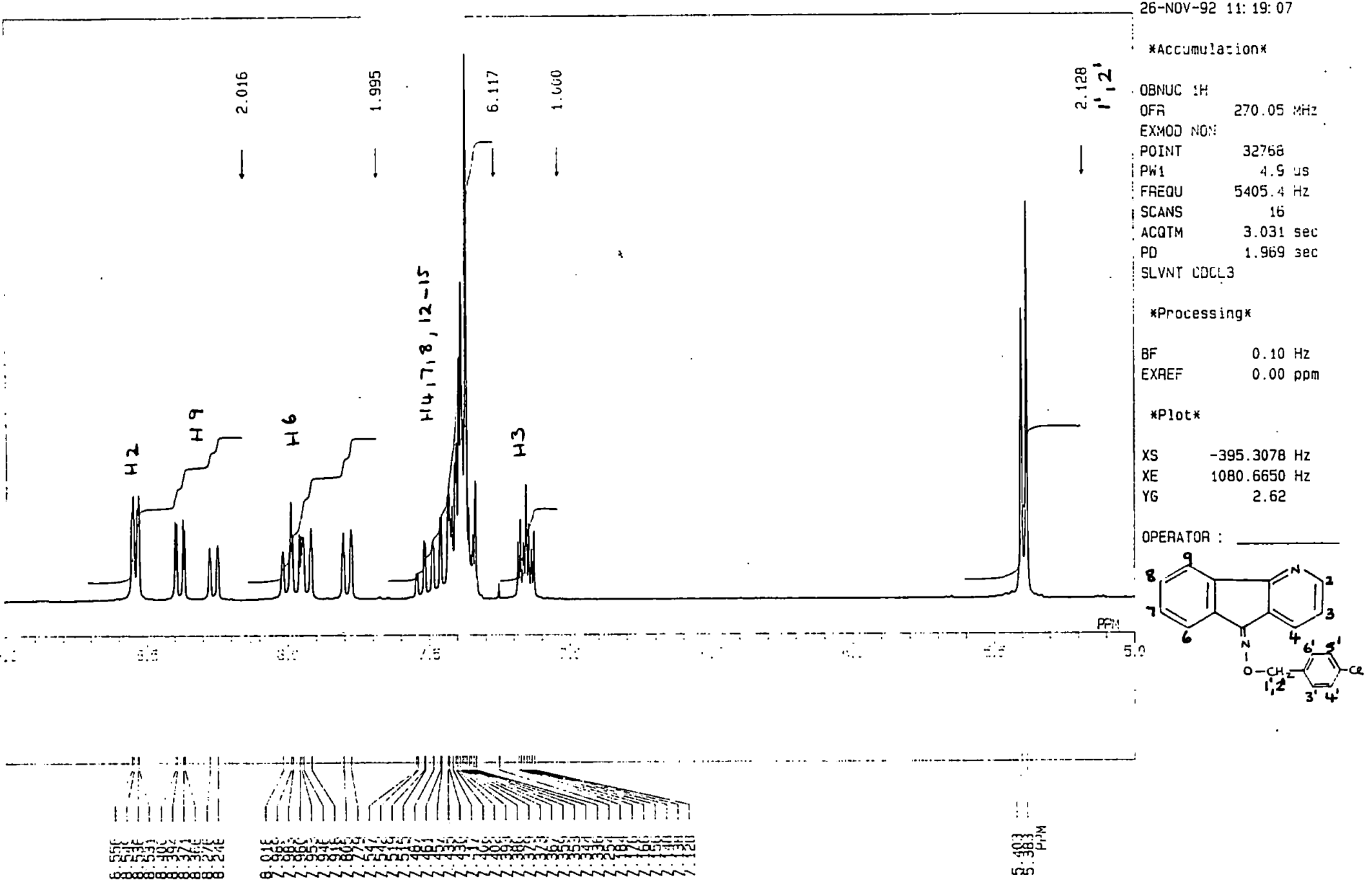
Appendix II.10

5H-indeno[1,2-b]pyridine-5-one 4-chlorobenzyloxime (225)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.5555	16.02778	2311.42	5720	+++
2		8.5494	18.99967	2309.77	5725	++++
3		8.5360	16.56471	2306.14	5736	+++
4		8.5311	19.10824	2304.82	5740	++++
5	H-2	8.4004	14.31312	2269.52	5847	+++
6		8.3943	13.91051	2267.87	5852	+++
7	H-9	8.3711	14.74454	2261.60	5871	+++
8		8.3663	12.73444	2260.28	5875	+++
9		8.2759	9.56987	2235.87	5949	++
10		8.2478	9.96197	2228.28	5972	++
11		8.0192	8.68012	2166.25	6160	++
12		7.9889	17.73148	2158.33	6184	++++
13		7.9828	11.47396	2156.69	6189	++
14	H-6	7.9596	11.89485	2150.42	6208	++
15		7.9535	11.51868	2148.77	6213	++
16		7.9462	11.38620	2146.79	6219	++
17		7.9181	12.96563	2139.20	6242	+++
18		7.8045	12.11092	2108.52	6335	++
19		7.7789	12.71759	2101.59	6356	+++
20		7.5468	4.65018	2038.90	6546	+
21		7.5420	4.73495	2037.58	6550	+
22		7.5188	10.73367	2031.32	6569	++
23		7.5151	10.25624	2030.33	6572	++
24		7.4870	10.60064	2022.74	6595	++
25		7.4614	14.92635	2015.81	6616	+++
26	H4	7.4565	14.84604	2014.49	6620	+++
27	H7	7.4345	18.62668	2008.55	6638	++++
28	H8	7.4296	19.15644	2007.23	6642	++++
29	H12	7.4174	16.89928	2003.93	6652	+++
30	H13	7.4064	24.66997	2000.96	6661	+++++
31	H14	7.4015	28.29565	1999.64	6665	++++++
32	H15	7.3930	43.74591	1997.33	6672	+++++++++
33		7.3857	57.43399	1995.35	6678	++++++++++
34		7.3795	32.40912	1993.71	6683	++++++
35		7.3734	34.14553	1992.06	6688	+++++++
36		7.3673	100.00000	1990.41	6693	++++++++++++++++++++
37		7.3588	16.58925	1988.10	6700	+++
38		7.3527	7.99947	1986.45	6705	++
39		7.3441	11.73426	1984.14	6712	++
40		7.3356	21.41709	1981.83	6719	++++
41		7.2538	2.80921	1959.72	6786	+
42		7.1642	10.54495	1940.92	6843	++
43		7.1756	14.56384	1938.61	6850	+++
44	H-3	7.1658	10.35417	1935.97	6858	++
45		7.1561	20.83372	1933.33	6866	++++
46		7.1475	13.77984	1931.02	6873	+++
47		7.1378	9.06432	1928.38	6881	++
48		7.1280	12.45891	1925.74	6889	++
49	H-1', 2'	5.4025	52.37722	1459.56	8302	++++++++++
50		5.3829	71.65913	1454.29	8318	+++++++++++++


26-NOV-92 11:19:07
Accumulation
OBNUC 1H
OFR 270.05 MHz
EXMOD NON
POINT 32768
PW1 4.9 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT CDCL3
Processing
BF 0.10 Hz
EXREF 0.00 ppm
Plot
XS -395.3078 Hz
XE 1080.6650 Hz
YG 2.62
OPERATOR :
2.016
1.995
6.117
1.000
2.128
1',2'
H2
H9
H6
H4,7,8,12-15
H3
PPM
5.403
5.383

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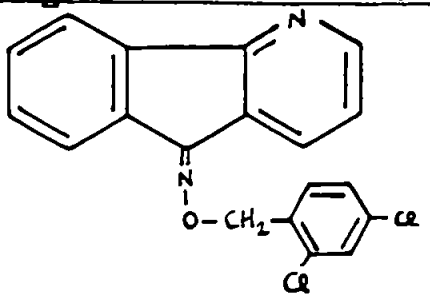
Appendix II.11

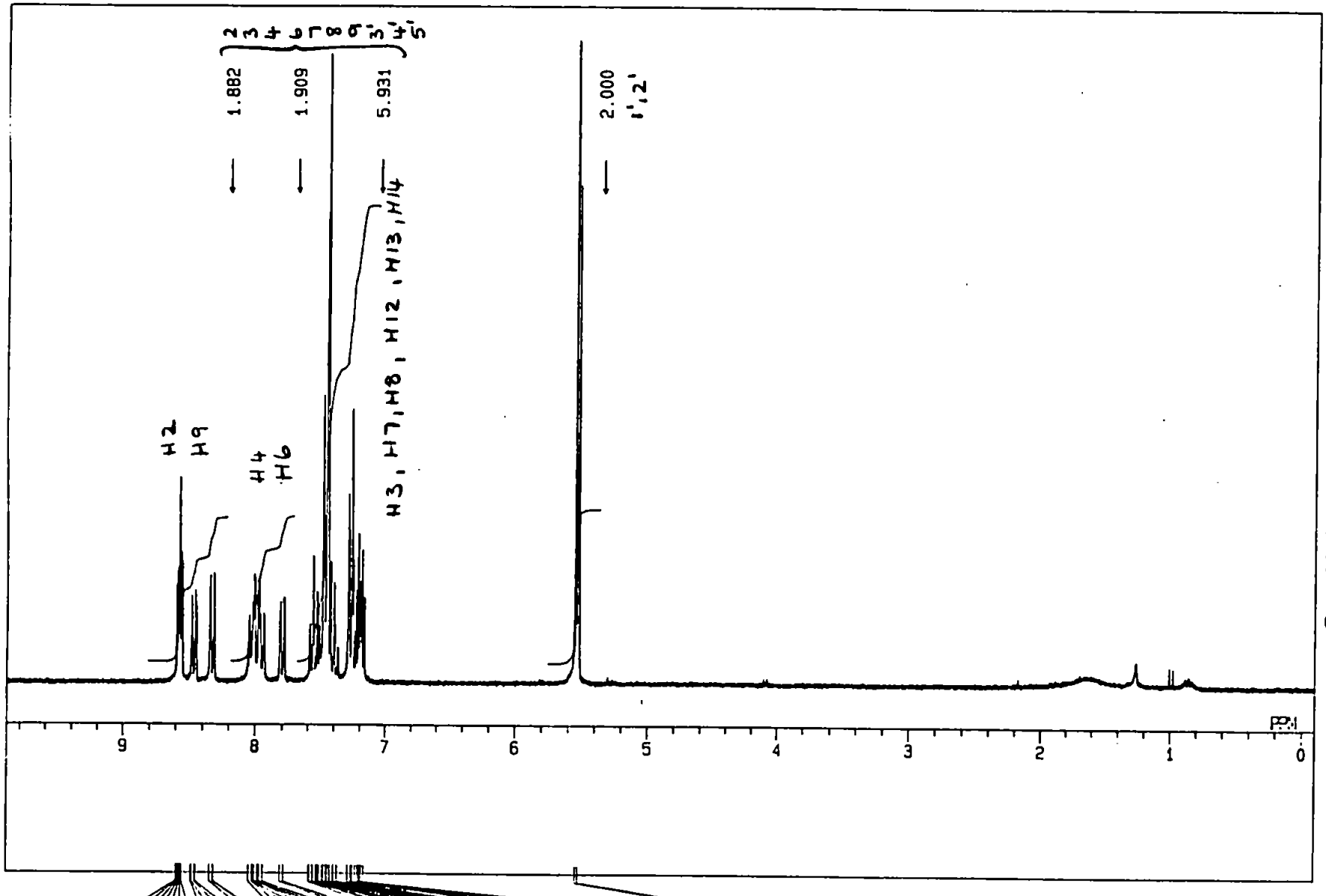
5H-indeno[1,2-b]pyridine-5-one 2,4-dichlorobenzyloxime (226)

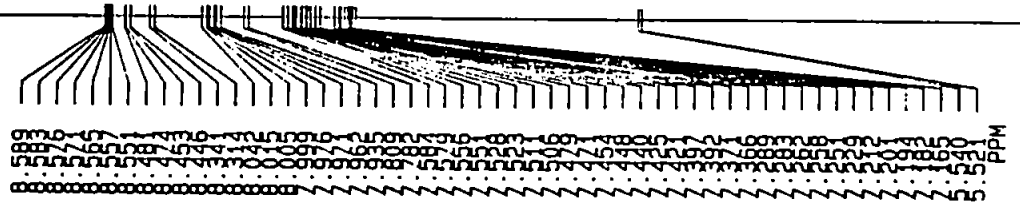


NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.5893	15.140E7	2320.53	5699	+++
2		8.5832	17.21796	2318.88	5704	+++
3		8.5758	20.99103	2316.90	5710	++++
4		8.5710	31.93718	2315.58	5714	++++
5		8.5648	17.66056	2313.93	5719	++++
6	H2	8.5575	20.15800	2311.95	5725	++++
7	H9	8.5514	18.42093	2310.30	5730	++++
8		8.4806	13.42945	2291.17	5788	+++
9		8.4745	12.05533	2289.52	5793	++
10		8.4525	14.29664	2283.58	5811	+++
11		8.4464	12.21700	2281.93	5816	++
12		8.3414	16.62362	2253.56	5902	+++
13		8.3145	16.96802	2246.30	5924	+++
14		8.0422	10.31780	2172.73	6147	++
15		8.0153	12.41944	2165.47	6169	++
16		8.0055	16.80698	2162.83	6177	+++
17	H4	7.9994	15.09260	2161.18	6182	+++
18	H6	7.9762	15.85722	2154.91	6201	+++
19		7.9714	16.06813	2153.59	6205	+++
20		7.9616	10.48746	2150.95	6213	++
21		7.9347	10.65988	2143.69	6235	++
22		7.8089	12.46575	2109.71	6338	++
23		7.7821	13.20265	2102.45	6360	+++
24		7.5842	8.19596	2049.01	6522	++
25		7.5794	8.80845	2047.69	6526	++
26		7.5712	11.06742	2045.48	6533	+++
27		7.5637	11.19777	2043.46	6540	+++
28		7.5281	14.15926	2033.83	6568	+++
29		7.5132	12.55150	2029.81	6580	+++
30		7.5110	8.16650	2029.21	6582	++
31		7.5061	8.78393	2027.89	6586	++
32		7.4792	44.73036	2020.63	6608	+++++ +++++
33		7.4707	22.45745	2018.32	6615	+++++
34		7.4636	72.26034	2016.71	6629	+++++++++++++++++
35		7.4475	97.90281	2012.06	6634	+++++++++++++++++++++++
36		7.4401	26.75669	2010.08	6640	+++++
37		7.4255	18.28979	2006.12	6652	++++
38		7.4206	18.73968	2004.80	6656	++++
39	H3	7.3974	18.54909	1998.53	6675	+++
40	H7	7.3925	17.64307	1997.21	6679	+++
41	H8	7.3708	5.44964	1991.37	6697	+
42		7.3657	5.28742	1989.98	6701	+
43	H12	7.2887	29.40298	1969.17	6764	++++++
44	H13	7.2826	20.91256	1967.52	6769	++++++
45	H14	7.2615	42.61951	1961.91	6786	++++++++++
46		7.2582	22.05433	1960.92	6789	++++
47		7.2509	19.02894	1958.94	6795	++++
48		7.2289	14.42269	1953.00	6813	+++
49		7.2118	27.25971	1948.38	6827	+++++
50		7.2008	13.62657	1945.41	6836	+++

Appendix II.11 (cont'd)

51		7.1935	15.76281	1943.43	6842	+++
52		7.1825	19.72177	1946.16	6851	++++
53		1.1674	15.22019	1725.84	6865	+++
54	H-1',2'	5.5402	170.20230	1496.72	8196	+++++++++++++++++++++++++
55		5.5205	77.57698	1491.44	8212	++++++++++++++++++++++++





03-SEP-91 11: 17: 07

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	5.0 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

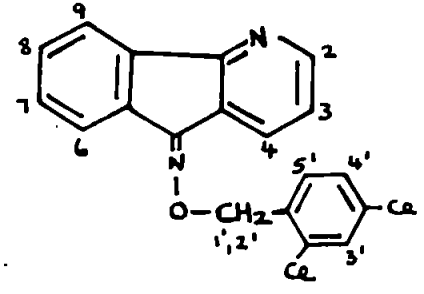
Processing

BF	0.10 Hz
EXREF	5.54 ppm

Plot

XS	174.2260 Hz
XE	2701.6630 Hz
YG	1.98

OPERATOR : _____



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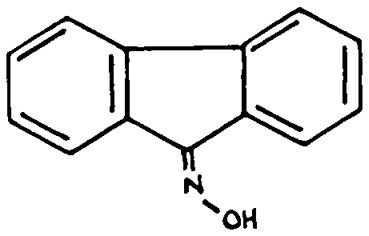
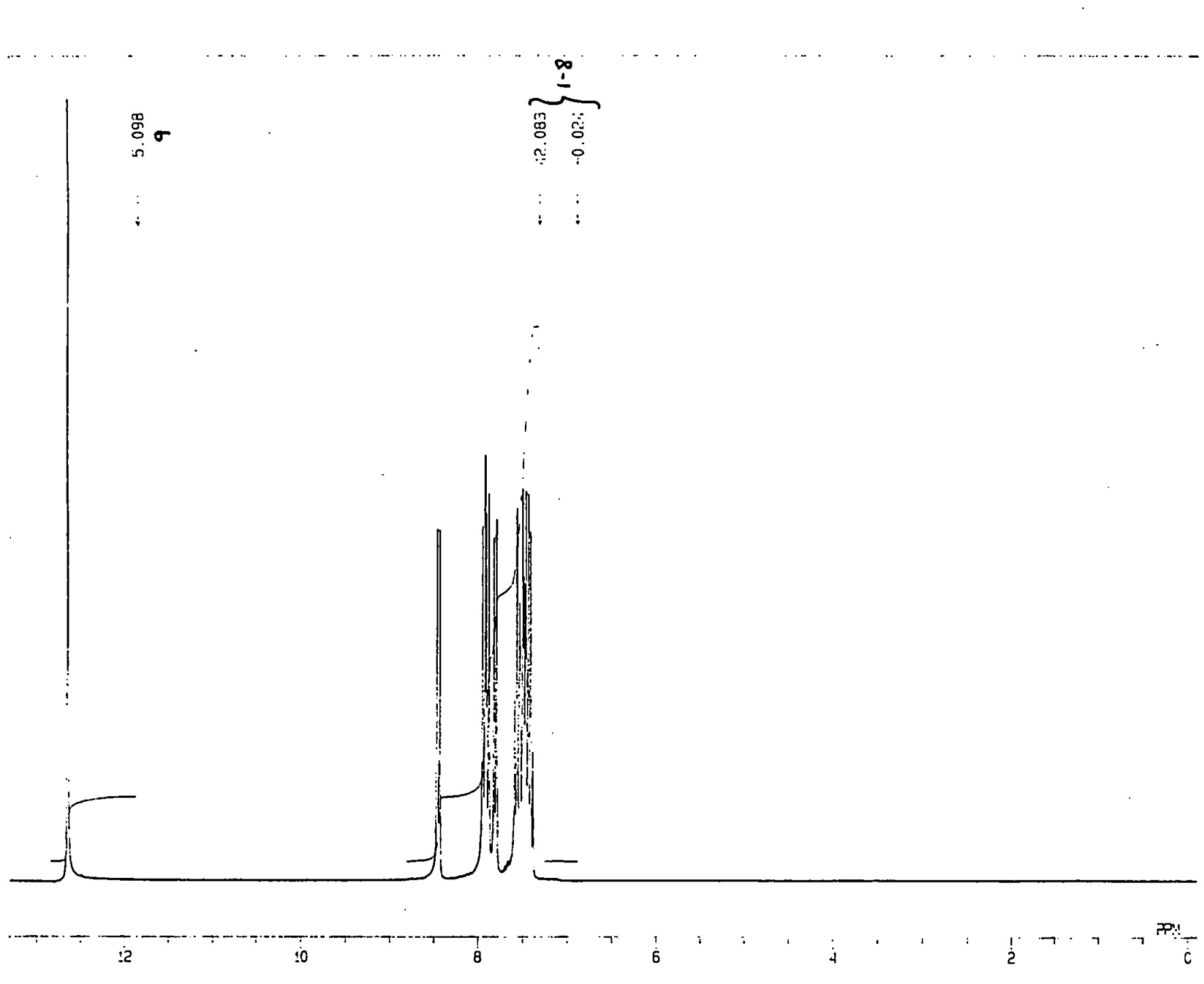
Appendix II.12

Fluorenone oxime (227)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		12.8129	-0.34457	3461.63	2045	
2	N-OH	12.6554	100.00000	3419.07	2174	++++++++++++++++++++
3		12.4979	0.65464	3376.51	2303	
4		8.4668	44.95979	2287.44	5604	+++++++++
5		8.4387	44.82914	2279.85	5627	+++++++++
6		8.2787	0.35735	2236.63	5758	
7		8.2482	0.45364	2228.39	5783	
8		8.2030	0.56671	2216.18	5820	
9		8.1762	0.64646	2208.92	5842	
10		8.1554	0.68463	2203.31	5859	
11		8.1236	0.89260	2194.73	5885	
12		8.0931	1.03580	2186.49	5910	
13		7.9515	45.38900	2148.22	6026	+++++++++
14		7.9234	54.42134	2140.63	6049	++++++++++
15		7.9087	46.95999	2136.67	6061	+++++++++
16		7.8806	49.48362	2129.08	6084	++++++++++
17		7.8232	43.86999	2113.57	6131	+++++++++
18		7.7951	46.18949	2105.99	6154	+++++++++
19		7.7304	1.24369	2088.50	6207	
20		7.7011	1.86083	2080.58	6231	
21		7.6742	2.41351	2073.32	6253	
22		7.6572	2.55978	2068.70	6267	+
23		7.5949	21.13673	2051.88	6318	++++
24		7.5912	23.06265	2050.89	6321	+++++
25		7.5668	46.55844	2044.29	6341	+++++++++
26		7.5631	47.67088	2043.30	6344	++++++++++
27		7.5387	33.72175	2036.70	6364	+++++++
28		7.5350	35.53237	2035.71	6367	+++++++
29		7.5314	29.96661	2034.72	6370	++++++
30		7.5265	26.16171	2033.40	6374	+++++
31		7.5021	49.18848	2026.80	6394	++++++++++
32		7.4984	50.14529	2025.82	6397	++++++++++
33		7.4911	39.44225	2023.84	6403	++++++++
34		7.4874	38.82217	2022.85	6406	++++++++
35		7.4752	37.96650	2019.55	6416	++++++++
36		7.4715	37.64967	2018.56	6419	++++++++
37		7.4630	49.82540	2016.25	6426	++++++++++
38		7.4593	49.47725	2015.26	6429	++++++++++
39		7.4398	39.41124	2009.98	6445	++++++++
40		7.4361	49.43985	2008.99	6448	++++++++++
41		7.4129	44.60059	2002.72	6467	+++++++++
42		7.4093	43.92548	2001.73	6470	+++++++++
43		7.3861	16.49335	1995.46	6489	+++
44		7.3824	16.10030	1994.47	6492	+++



11-NOV-92 15:25:43

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NOE
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SOLVNT	DMSO

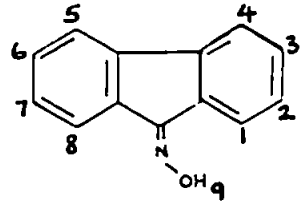
Processing

BF	0.10 Hz
EXREF	2.49 ppm

Plot

XS	-351.8380 Hz
XE	3624.9270 Hz
YG	2.55

OPERATOR : _____



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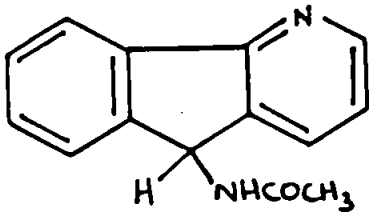
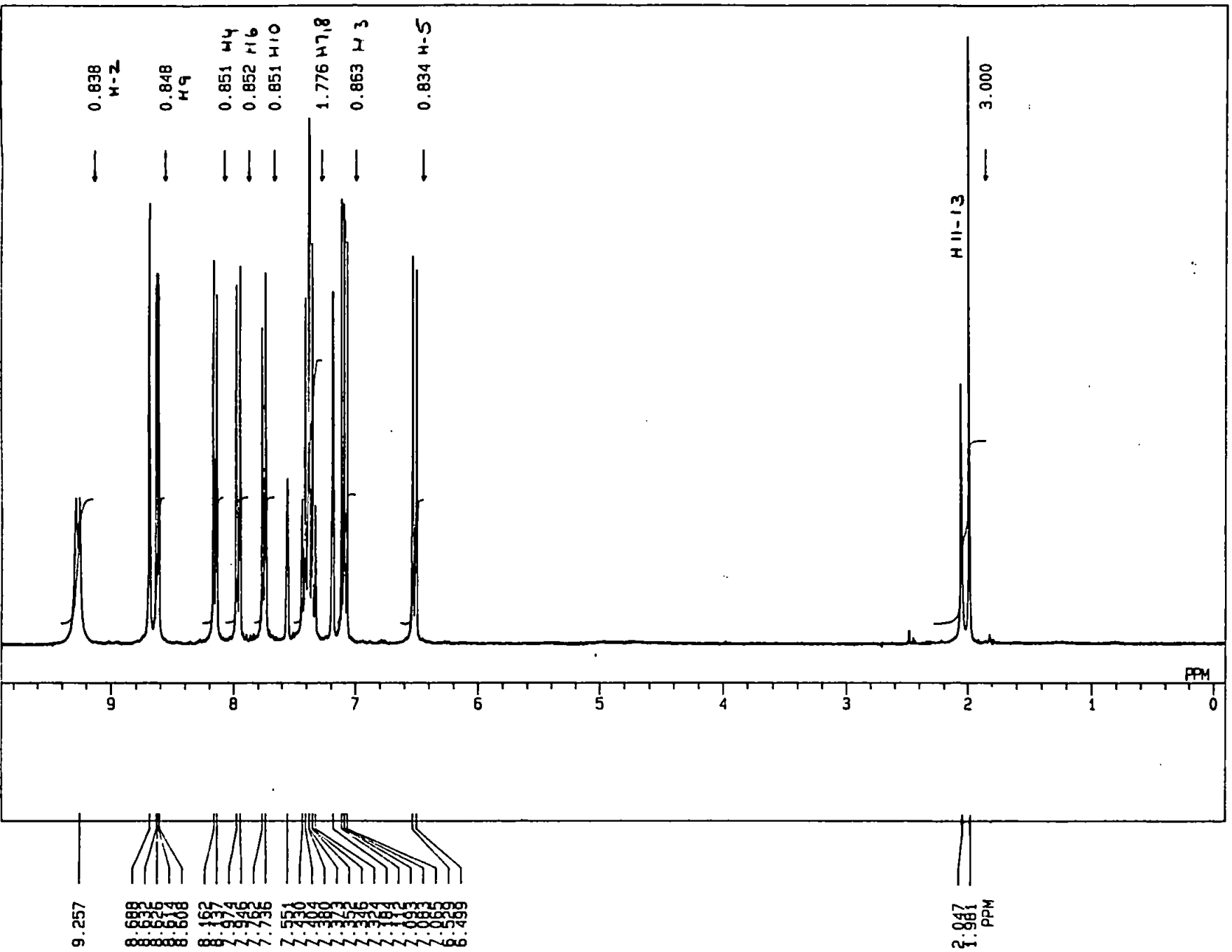
Appendix II.13

5-acetamido,5H-indeno[1,2-b]pyridine (230)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H-2	9.2572	3.03025	2500.99	3931	+
2		x 8.6881	9.17722	2347.24	4397	++
3		8.6320	7.45041	2332.07	4443	+
4		8.6259	7.71516	2330.42	4448	++
5	H-9	8.6136	7.69876	2327.12	4458	++
6		8.6075	7.44970	2325.47	4463	+
7		8.1610	7.98360	2205.05	4828	++
8	H4	8.1374	7.27252	2198.45	4848	+
9	H6	7.9737	7.46262	2154.24	4982	+
10	H10	7.9457	7.85839	2146.65	5005	++
11		7.7625	6.50478	2097.16	5155	+
12		7.7356	7.72504	2089.91	5177	++
13		x 7.5512	3.42349	2040.09	5328	+
14		7.4303	2.98788	2007.43	5427	+
15		7.4035	7.18884	2000.17	5449	+
16	H-7	7.3803	10.96504	1993.90	5468	++
17	H-8	7.3729	10.59551	1991.92	5474	++
18		7.3522	8.33962	1986.31	5491	++
19		7.3461	7.13009	1984.66	5496	+
20		7.3241	2.85984	1978.72	5514	+
21		x 7.1836	7.32877	1940.78	5629	+
22		7.1116	9.26167	1921.32	5686	++
23	H-3	7.0933	9.16129	1916.37	5703	++
24		7.0835	8.81755	1913.73	5711	++
25		7.0652	8.36481	1908.78	5726	++
26	H-5	6.5291	8.07702	1763.95	6165	++
27		6.4986	7.78688	1755.70	6190	++
28	H-11,12	2.0469	42.90302	553.02	10788	+++++++++
29	H-13	1.9810	100.00000	535.20	10842	++++++++++++++++++++



20-JAN-93 10:26:44

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	C5D5N

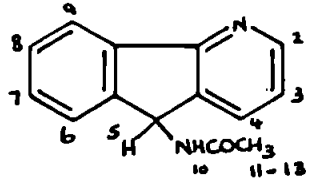
Processing

BF	0.10 Hz
EXREF	7.55 ppm

Plot

XS	-228.6188 Hz
XE	2701.6670 Hz
YG	18.96

OPERATOR : _____



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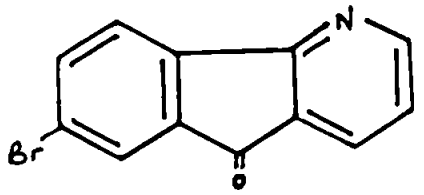
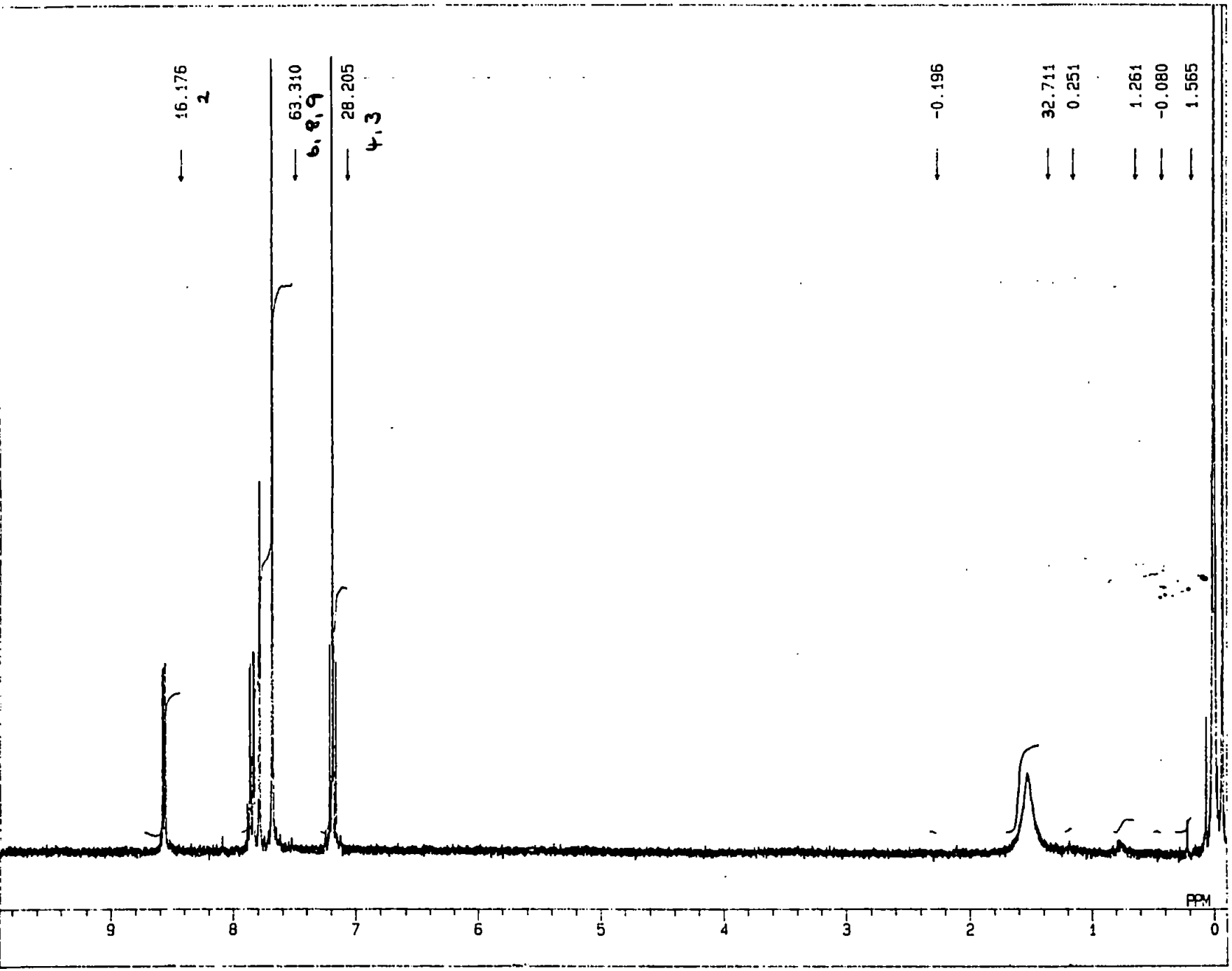
Appendix II.14

7-bromo-5H-indeno[1,2-b]pyridine-5-one (233).



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H-2	8.5787	1.90510	2317.69	5650	
2		8.5739	1.96700	2316.37	5654	
3		8.5604	1.96964	2312.74	5665	
4		8.5543	2.02426	2311.09	5670	
5		8.0793	0.41955	2182.75	6059	
6		7.8839	0.50803	2129.96	6219	
7		7.8656	1.96492	2125.01	6234	
8		7.8595	2.01330	2123.36	6239	
9	H6	7.8497	0.34354	2120.72	6247	
10	H8	7.8375	2.14390	2117.43	6257	
11	H9	7.8314	2.13541	2115.78	6262	
12		7.7911	2.01197	2104.89	6295	
13		7.7862	3.96291	2103.57	6299	+
14		7.7825	2.48199	2102.58	6302	
15		7.6861	8.47617	2076.51	6381	++
16		7.6812	7.02387	2075.20	6385	+
17	H4	7.2122	2.21511	1948.51	6769	
18		7.1927	8.57691	1943.23	6785	++
19	H3	7.1842	2.19859	1940.92	6792	
20		7.1658	2.02954	1935.97	6807	
21		1.5314	0.82424	413.72	11421	
22		1.5277	0.84397	412.73	11424	
23		0.2174	0.33127	58.73	12497	
24		0.0684	0.34361	18.48	12619	
25		0.0623	1.43810	16.83	12624	
26		0.0293	0.56530	7.92	12651	
27		0.0134	4.05741	3.63	12664	+
28		0.0000	100.00000	0.00	12675	++++++++++++++++++++



EX270
20-JUN-91 13:50:34

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.8 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

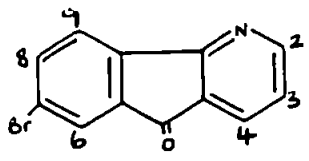
Processing

BF	0.10 Hz
EXREF	0.00 ppm

Plot

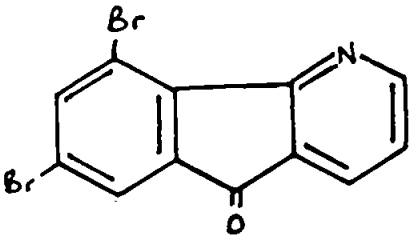
XS	155.2153 Hz
XE	2701.6630 Hz
YG	34.86

OPERATOR : _____

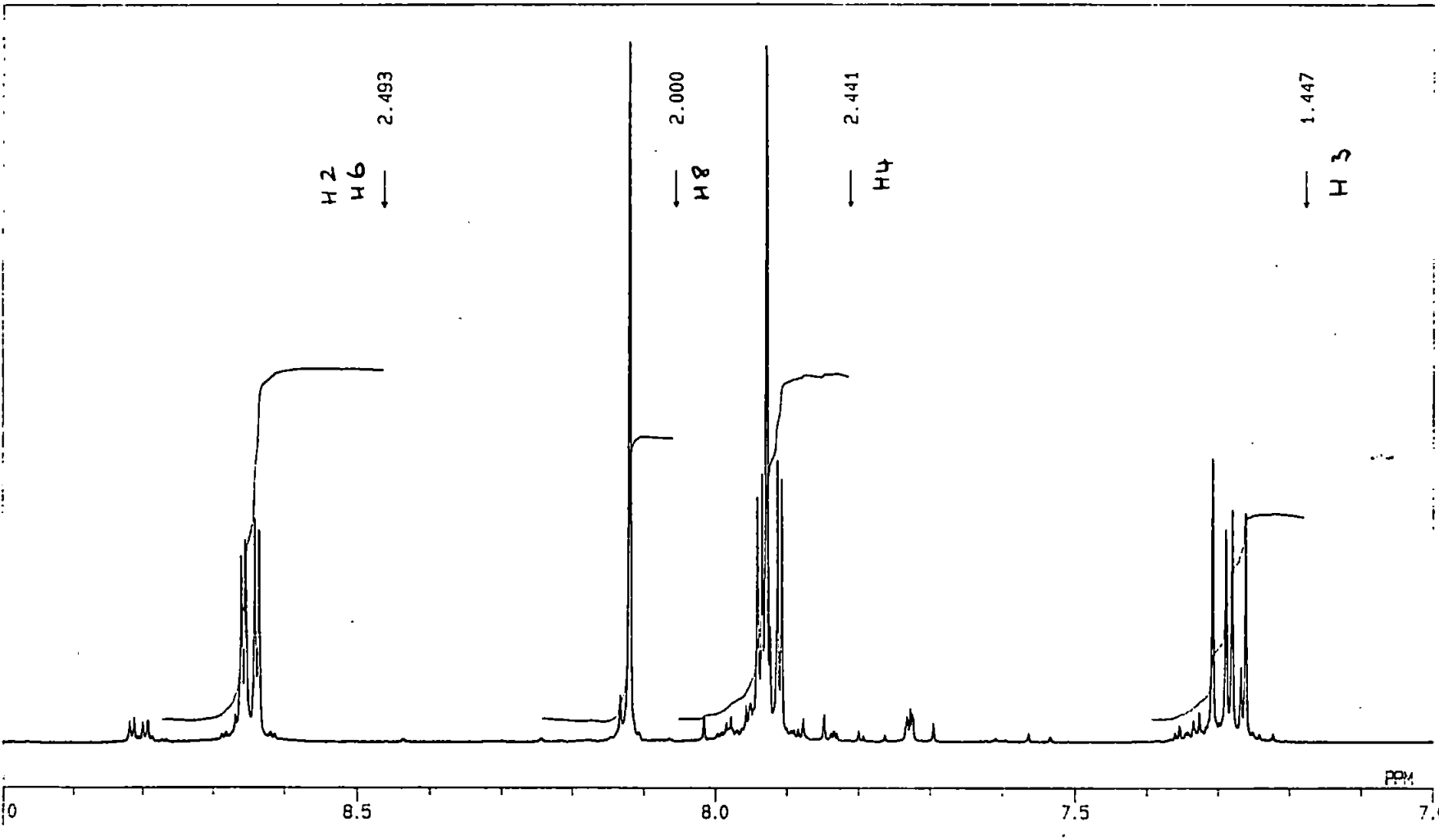


Appendix II.15

7,9-dibromo-5H-indeno[1,2-b]pyridine-5-one (234)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.8181	3.07427	2382.35	5516	+
2		8.8120	3.62284	2380.70	5521	+
3	H2	8.7998	2.92787	2377.40	5531	+
4	H6	8.7924	3.17321	2375.42	5537	+
5		8.6813	1.60332	2345.40	5628	
6		8.6691	4.07526	2342.10	5638	+
7		8.6606	26.71445	2339.79	5645	+++++
8		8.6345	29.07407	2338.14	5650	++++++
9		8.6410	32.01607	2334.51	5661	++++++
10		8.6349	30.39710	2332.86	5666	++++++
11		8.6190	1.48302	2328.57	5679	
12	H-8	8.1330	6.71378	2197.27	6077	+
13		8.1196	100.00000	2193.64	6088	++++++++++++++++++++
14		8.0158	3.53395	2165.59	6173	+
15		7.9840	2.89850	2157.02	6199	+
16		7.9779	3.75938	2155.37	6204	+
17		7.9694	1.86169	2153.06	6211	
18		7.9572	5.25336	2149.76	6221	+
19		7.9511	5.62825	2148.11	6226	+
20		7.9413	35.06225	2145.47	6234	+++++++
21		7.9352	38.39750	2143.82	6239	++++++++
22		7.9291	99.48508	2142.17	6244	++++++++++++++++++++
23		7.9230	16.66591	2140.52	6249	+++
24		7.9132	40.31441	2137.88	6257	++++++++
25		7.9071	37.61375	2136.23	6262	++++++++
26		7.8900	1.83011	2131.61	6276	
27	H4	7.8839	1.94569	2129.96	6281	
28		7.8766	3.46877	2127.98	6287	+
29		7.8473	3.96038	2120.06	6311	+
30		7.8387	1.26778	2117.75	6318	
31		7.8338	1.70277	2116.44	6322	
32		7.8302	1.28600	2115.45	6325	
33		7.7996	1.68572	2107.20	6350	
34		7.7325	3.77114	2089.05	6405	+
35		7.7276	4.81501	2087.73	6409	+
36		7.7251	4.05216	2087.07	6411	+
37		7.6958	2.84117	2079.15	6435	+
38		7.5627	1.33798	2043.19	6544	
39		7.3600	1.39530	1988.43	6710	
40		7.3539	2.46508	1986.78	6715	
41		7.3417	1.55180	1983.48	6725	
42	H3	7.3344	3.20977	1981.50	6731	+
43		7.3258	4.34669	1979.19	6738	+
44		7.3075	40.61551	1974.24	6753	++++++++
45		7.2892	30.49372	1969.29	6768	++++++
46		7.2794	33.31607	1966.65	6776	+++++++
47		7.2672	10.83164	1963.35	6786	++
48		7.2611	32.82169	1961.70	6791	+++++++
49		7.2232	1.26045	1951.48	6822	



26-NOV-92 09:40:33

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

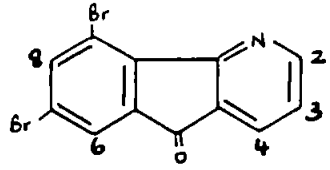
Processing

BF	0.10 Hz
EXREF	0.00 ppm

Plot

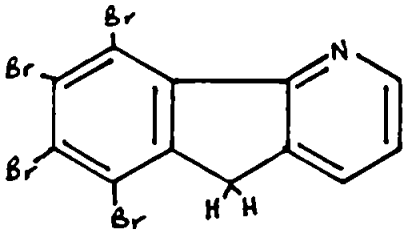
XS	-661.6450 Hz
XE	540.3325 Hz
YG	3.00

OPERATOR : _____

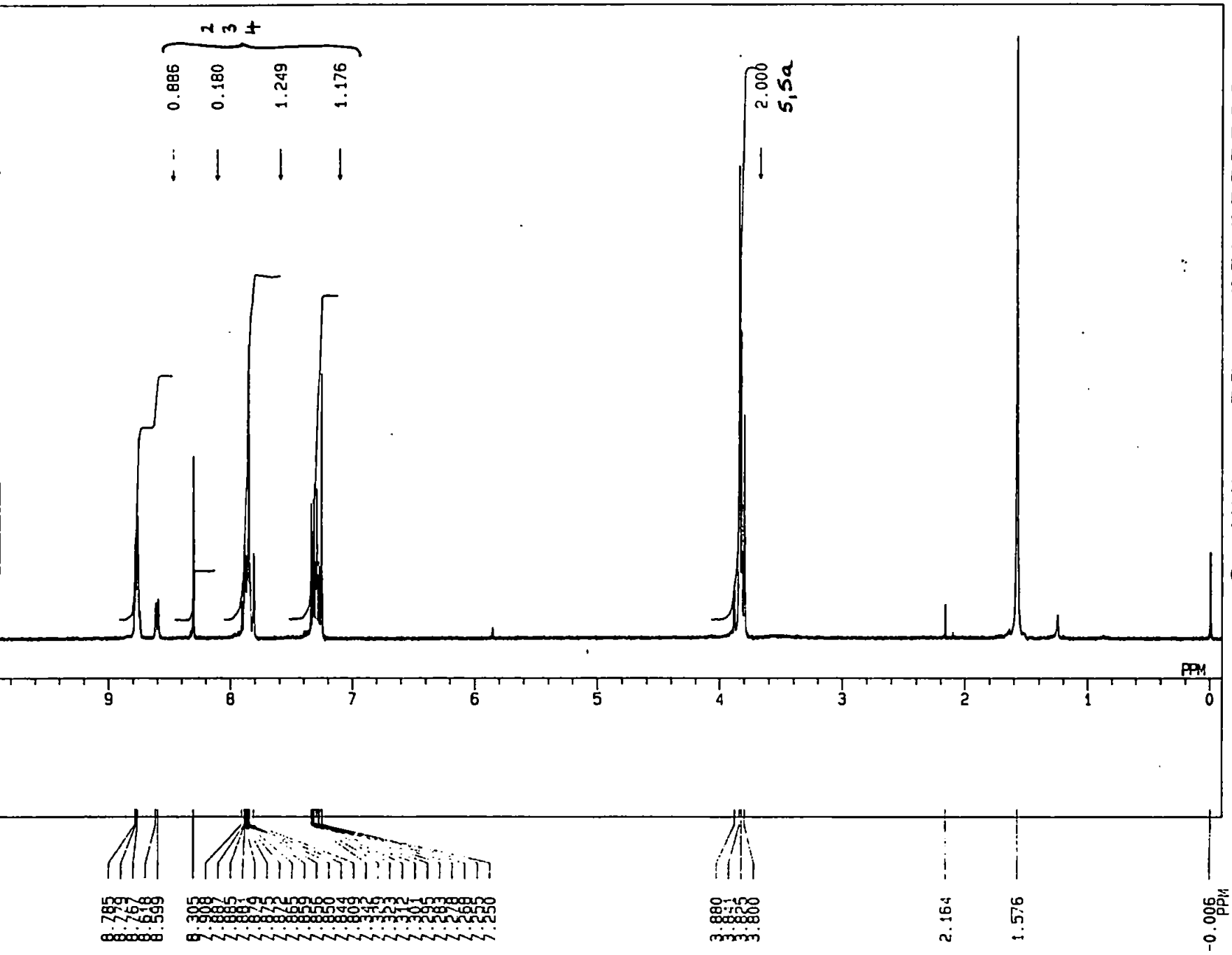


Appendix II.16

Tetrabromo-5H-indeno[1,2-b]pyridine (237)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.7850	16.49549	2373.41	5532	+++
2		8.7789	14.38755	2371.77	5537	+++
3	H-2	8.7667	20.26602	2368.47	5547	++++
4		8.6177	5.80483	2328.22	5669	+
5		8.5994	6.37383	2323.27	5684	+
6		8.3051	30.23502	2243.76	5925	++++++
7		7.9082	5.84164	2136.53	6250	+
8		7.8875	11.62038	2130.92	6267	++
9		7.8850	14.99791	2130.26	6269	+++
10		7.8813	12.83365	2129.27	6272	+++
11		7.8789	13.52072	2128.61	6274	+++
12		7.8752	10.67186	2127.62	6277	++
13		7.8716	10.34992	2126.63	6280	++
14	H3	7.8655	13.53882	2124.99	6285	+++
15		7.8594	14.78920	2123.34	6290	+++
16		7.8557	18.73250	2122.35	6293	++++
17		7.8496	48.75150	2120.70	6298	++++++++++
18		7.8435	12.33126	2119.05	6303	++
19		7.8093	13.99806	2109.81	6331	+++
20		7.3416	22.40512	1983.45	6714	++++
21		7.3294	11.29640	1980.15	6724	++
22		7.3233	23.01099	1978.50	6729	+++++
23		7.3123	25.50546	1975.53	6738	+++++
24		7.3013	12.45378	1972.56	6747	++
25	H4	7.2952	24.77085	1970.91	6752	+++++
26		7.2830	10.25396	1967.61	6762	++
27		7.2781	12.71645	1966.29	6766	+++
28		7.2683	11.70910	1963.65	6774	++
29		7.2549	43.91347	1960.03	6785	+++++++++
30		7.2500	10.15677	1958.71	6789	++
31		3.8796	7.76585	1048.13	9549	++
32	H5	3.8405	78.60983	1037.57	9581	++++++++++++++++
33	H5a	3.8246	51.03071	1033.28	9594	++++++++++
34		3.8002	37.19788	1026.68	9614	+++++++
35		2.1638	5.47395	584.59	10954	+
36		1.5764	100.00000	425.90	11435	++++++++++++++++++++
37		-0.0062	14.16632	-1.68	12731	+++



29-APR-93 10: 40: 47

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

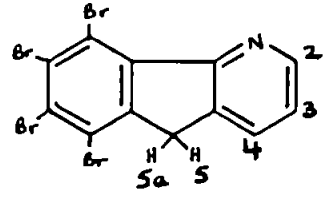
Processing

BF	0.10 Hz
EXREF	7.25 ppm

Plot

XS	172.0133 Hz
XE	2701.6630 Hz
YG	3.64

OPERATOR : _____



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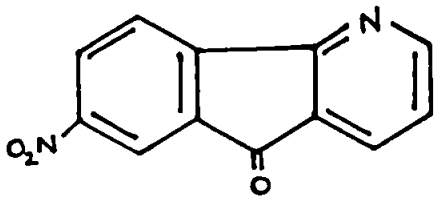
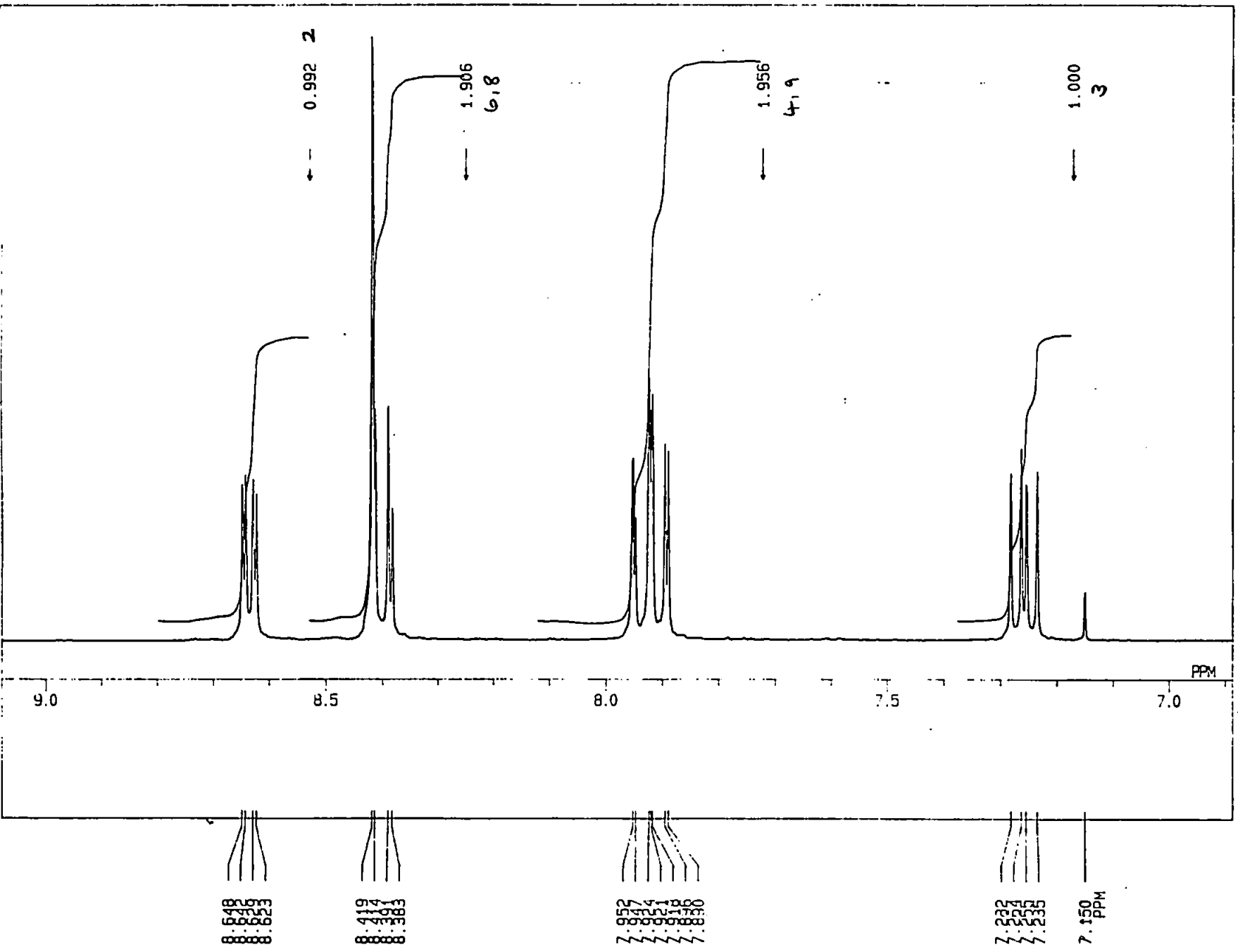
Appendix II.17

7-nitro-5H-indeno[1,2-b]pyridine-5-one (238)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.6484	25.85498	2336.50	5558	+++++
2	H-2	8.6423	27.28915	2334.85	5563	+++++
3		8.6288	26.65657	2331.22	5574	+++++
4		8.6227	24.27773	2329.57	5579	+++++
5		8.4188	100.00000	2274.48	5746	++++++++++++++++++++
6	H-6	8.4139	38.31920	2273.16	5750	++++++++
7	H-8	8.3907	38.81635	2266.89	5769	++++++++
8		8.3834	21.82227	2264.91	5775	++++
9		7.9523	30.15823	2148.45	6128	++++++
10		7.9474	20.18733	2147.13	6132	++++
11	H-4	7.9242	43.38789	2140.86	6151	+++++++++
12	H-9	7.9206	38.03481	2139.87	6154	++++++++
13		7.9161	40.77868	2139.21	6156	++++++++
14		7.8961	32.59158	2133.27	6174	+++++++
15		7.8900	31.43801	2131.62	6179	++++++
16		7.2819	27.72923	1967.32	6677	++++++
17		7.2636	31.82415	1962.37	6692	++++++
18	H-3	7.2550	25.86652	1960.06	6699	+++++
19		7.2355	28.03560	1954.78	6715	++++++
20		7.1500	8.03737	1931.69	6785	++



21-APR-93 10: 41: 28

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

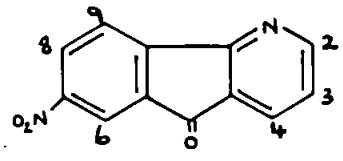
Processing

BF	0.10 Hz
EXREF	7.15 ppm

Plot

XS	-689.4062 Hz
XE	592.3079 Hz
YG	2.69

OPERATOR : _____



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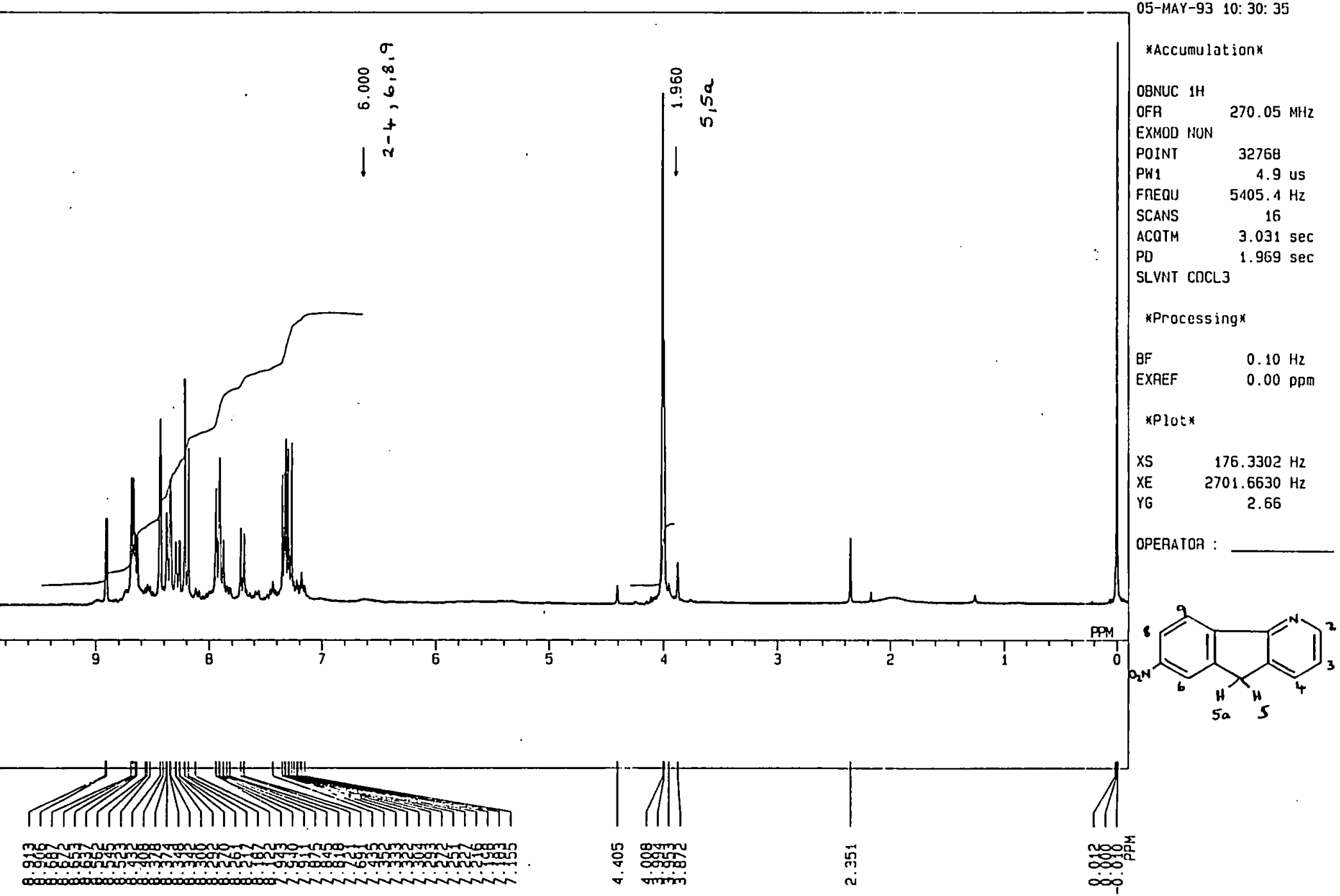
Appendix II. 18

7-nitro-5H-indeno [1,2-b] pyridine (239)

$C_{12}H_8N_2O_2$ ($CDCl_3$)

NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.9133	15.27230	2408.08	5440	+++
2		8.9060	15.30124	2406.10	5446	+++
3		8.6874	22.52879	2347.05	5625	+++++
4		8.6715	22.47842	2342.76	5638	++++
5		8.6532	12.68841	2337.81	5653	+++
6		8.6374	12.11956	2333.52	5666	++
7		8.5616	2.93021	2313.07	5728	+
8		8.5445	3.56923	2308.45	5742	+
9		8.5226	3.29711	2302.51	5760	+
10		8.4322	33.00813	2278.10	5834	+++++++
11		8.4078	3.11980	2271.50	5854	+
12		8.3785	16.35902	2263.58	5878	+++
13		8.3736	13.65532	2262.26	5882	+++
14		8.3479	22.15224	2255.33	5903	++++
15		8.3418	19.75987	2253.68	5908	++++
16		8.3003	11.14034	2242.46	5942	++
17		8.2918	10.72544	2240.16	5949	++
18		8.2698	11.42979	2234.22	5967	++
19		8.2612	11.13509	2231.91	5974	++
20		8.2173	40.16426	2220.03	6010	++++++++
21		8.1867	27.74835	2211.78	6035	++++++
22		8.1220	2.85997	2194.30	6088	+
23		7.9425	20.54955	2145.80	6235	++++
24		7.9401	20.15671	2145.14	6237	++++
25		7.9108	26.09682	2137.22	6261	+++++
26		7.8753	11.31932	2127.65	6290	++
27		7.8448	3.22980	2119.40	6315	+
28		7.8179	2.98001	2112.15	6337	+
29		7.7215	13.52963	2086.08	6416	+++
30		7.6909	12.53052	2077.83	6441	+++
31		7.4345	4.02974	2008.55	6651	+
32		7.3515	23.00417	1986.12	6719	+++++
33		7.3331	23.30016	1981.17	6734	+++++
34		7.3222	29.37192	1978.20	6743	++++++
35		7.3038	27.55274	1973.25	6758	++++++
36		7.2928	11.76558	1970.28	6767	++
37		7.2721	28.66791	1964.67	6784	++++++
38		7.2513	4.02522	1959.06	6801	+
39		7.2269	4.37369	1952.47	6821	+
40		7.2159	3.40942	1949.50	6830	+
41		7.1976	3.21746	1944.55	6845	+
42		7.1829	5.74785	1940.59	6857	+
43		7.1549	3.31710	1933.00	6880	+
44		4.4048	3.25394	1190.02	9132	+
45		4.0079	91.03654	1082.80	9457	++++++++++++++++++
46	H-5	3.9945	47.10418	1079.17	9468	+++++++++
47	H-5a	3.9529	3.73984	1067.95	9502	+
48		3.8723	7.43879	1046.18	9568	+
49		2.3508	11.68531	635.10	10814	++
50		0.0122	6.76791	3.30	12729	+
51		0.0000	100.00000	0.00	12739	++++++++++++++++++++
52		-0.0098	4.36850	-2.64	12747	+



05-MAY-93 10: 30: 35

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

Processing

BF	0.10 Hz
EXREF	0.00 ppm

Plot

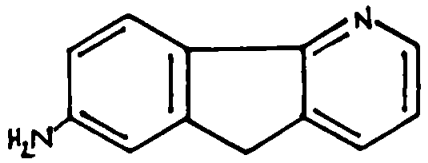
XS	176.3302 Hz
XE	2701.6630 Hz
YG	2.66

OPERATOR : _____

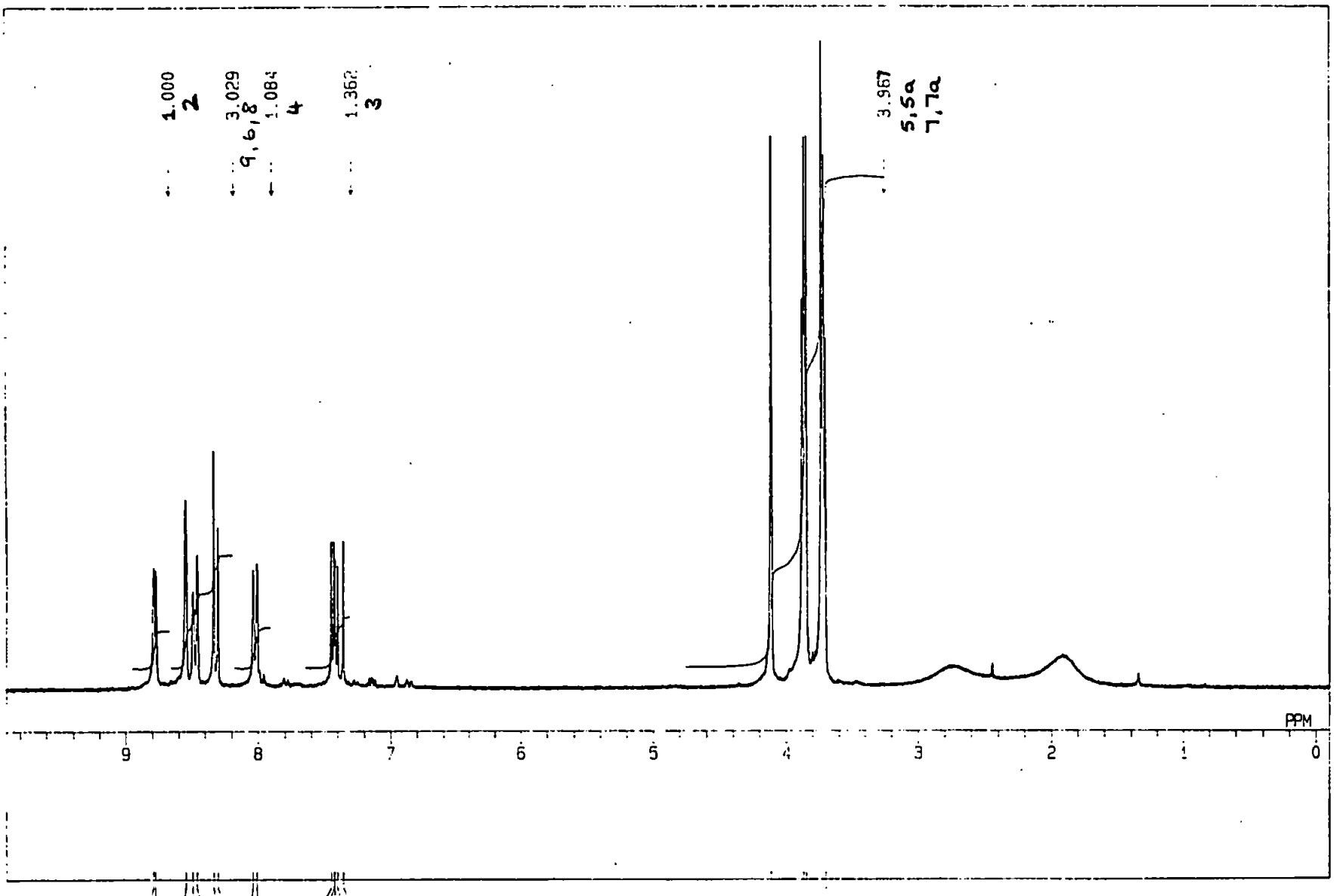
320

Appendix II.19

7-emino-5H-indeno[1,2-b]pyridine (240)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H-2	8.7923	18.58744	2375.39	5610	++++
2		8.7765	18.12932	2371.11	5623	++++
3		8.5457	29.18095	2308.75	5812	++++++
4	H9	8.4919	14.93100	2294.23	5856	+++
5	H6	8.4602	20.57690	2285.66	5882	++++
6	H8	8.3356	36.79622	2252.00	5984	+++++++
7		8.3039	24.89699	2243.43	6010	+++++
8	H4	8.0389	18.22565	2171.83	6227	++++
9		8.0108	19.25456	2164.25	6250	++++
10		7.4478	22.64627	2012.15	6711	+++++
11		7.4295	22.61236	2007.20	6726	+++++
12	H3	7.4197	19.83093	2004.56	6734	++++
13		7.4014	18.90252	1999.62	6749	++++
14		7.3575	22.70473	1987.74	6785	+++++
15		4.1128	85.36670	1111.14	9442	-++++++++++++++++
16	H5,5a	3.8820	60.17640	1048.79	9631	++++++++++++
17		3.8661	85.24413	1044.50	9644	+++++++++++++++++
18	H7,7a	3.8490	85.38322	1039.88	9658	+++++++++++++++++
19		3.7367	100.00000	1009.53	9750	++++++++++++++++++++
20		3.7196	82.51157	1004.91	9764	+++++++++++++++++
21		3.7037	54.07333	1000.62	9777	++++++++++



21-APR-93 14:38:02

Accumulation

OBNUC 1H
OFR 270.05 MHz
EXNUC NUC
POINT 32766
PW1 5.0 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT CDCL3

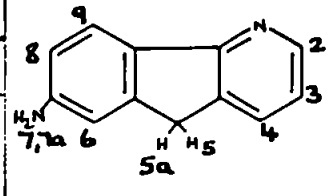
Processing

BF 0.10 Hz
EXREF 7.25 ppm

Plot

XS 199.7267 Hz
XE 2701.6620 Hz
YG 3.24

OPERATOR : _____



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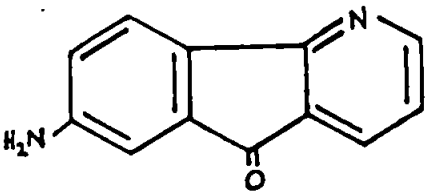
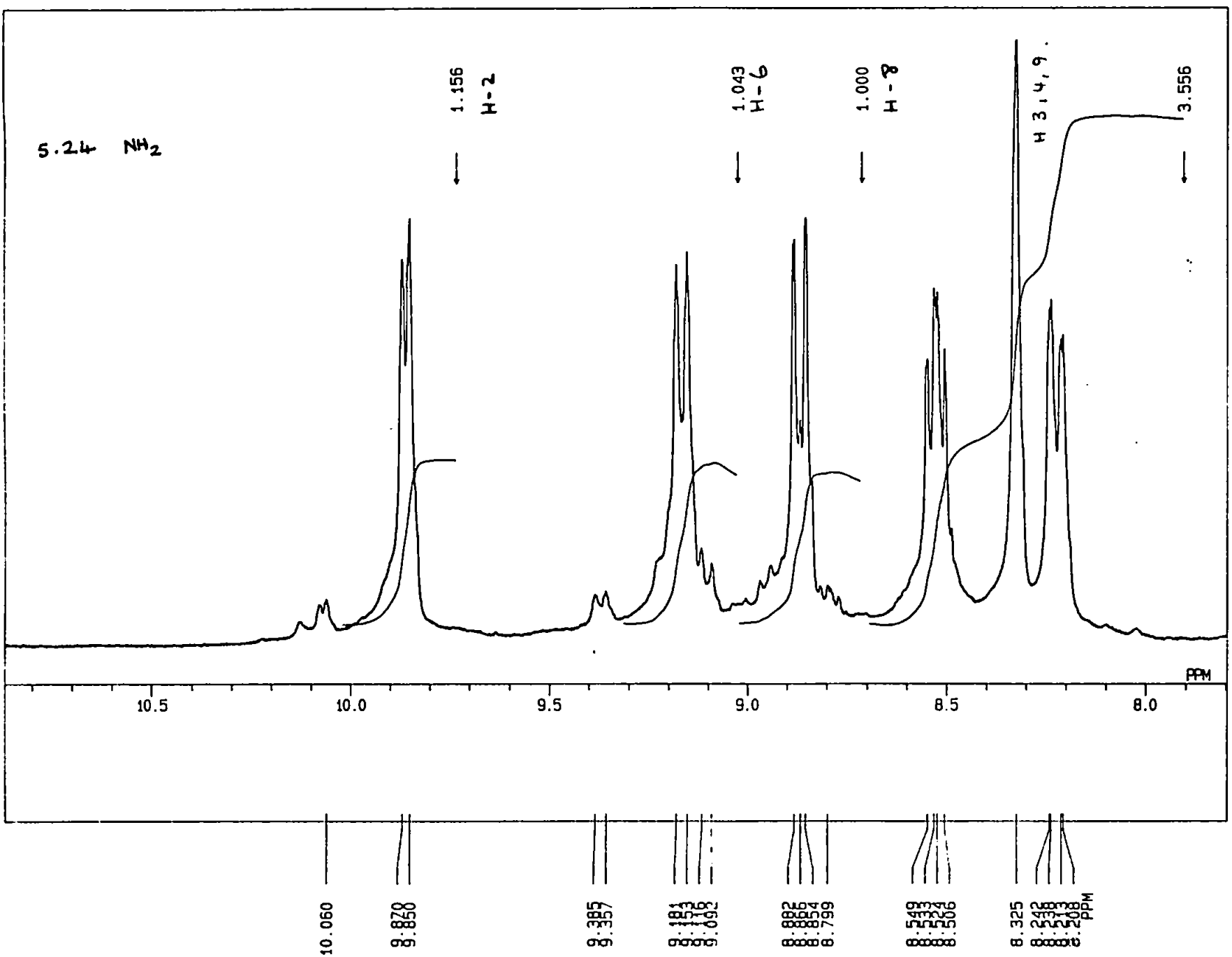
Appendix II.20

7-amino-5H-indeno[1,2-b]pyridin-5-one (241)



.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	10.0603	2.59436	2717.95	5429	+
2	9.8698	21.23759	2666.48	5585	++++
3	9.8502	23.46532	2661.20	5601	+++++
4	9.3850	2.82667	2535.50	5982	+
5	9.3569	2.99618	2527.91	6005	+
6	9.1810	20.90730	2480.41	6149	++++
7	9.1530	21.57787	2472.82	6172	++++
8	9.1163	5.35937	2462.92	6202	+
9	9.0919	4.53548	2456.32	6222	+
0	8.8819	22.26284	2399.58	6394	++++
1	8.8660	12.36814	2395.29	6407	++
2	8.8535	23.48531	2391.99	6417	+++++
3	8.7965	3.32749	2377.14	6462	+
4	8.5485	15.74202	2309.51	6667	+++
5	8.5326	19.60613	2305.22	6680	++++
6	8.5241	19.38271	2302.91	6687	++++
7	8.5057	16.28212	2297.96	6702	+++
8	8.3250	33.16289	2249.13	6850	+++++++
9	8.2420	18.48677	2226.70	6918	++++
0	8.2360	18.99432	2225.71	6921	++++
1	8.2127	16.84107	2218.78	6942	+++
2	8.2078	17.05532	2217.46	6946	+++
3	7.4213	15.45764	2004.99	7590	+++
4	5.2415	100.00000	1416.09	9375	++++++++++++++++++++



15-JAN-93 13: 30: 28

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

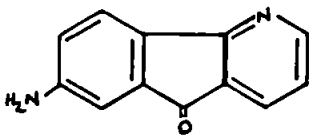
Processing

BF	0.10 Hz
EXREF	2.50 ppm

Plot

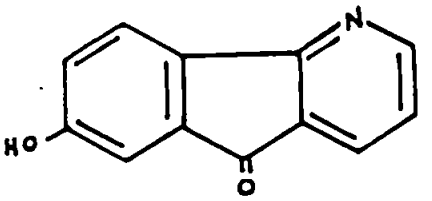
XS	-715.2661 Hz
XE	830.0781 Hz
YG	9.51

OPERATOR : _____

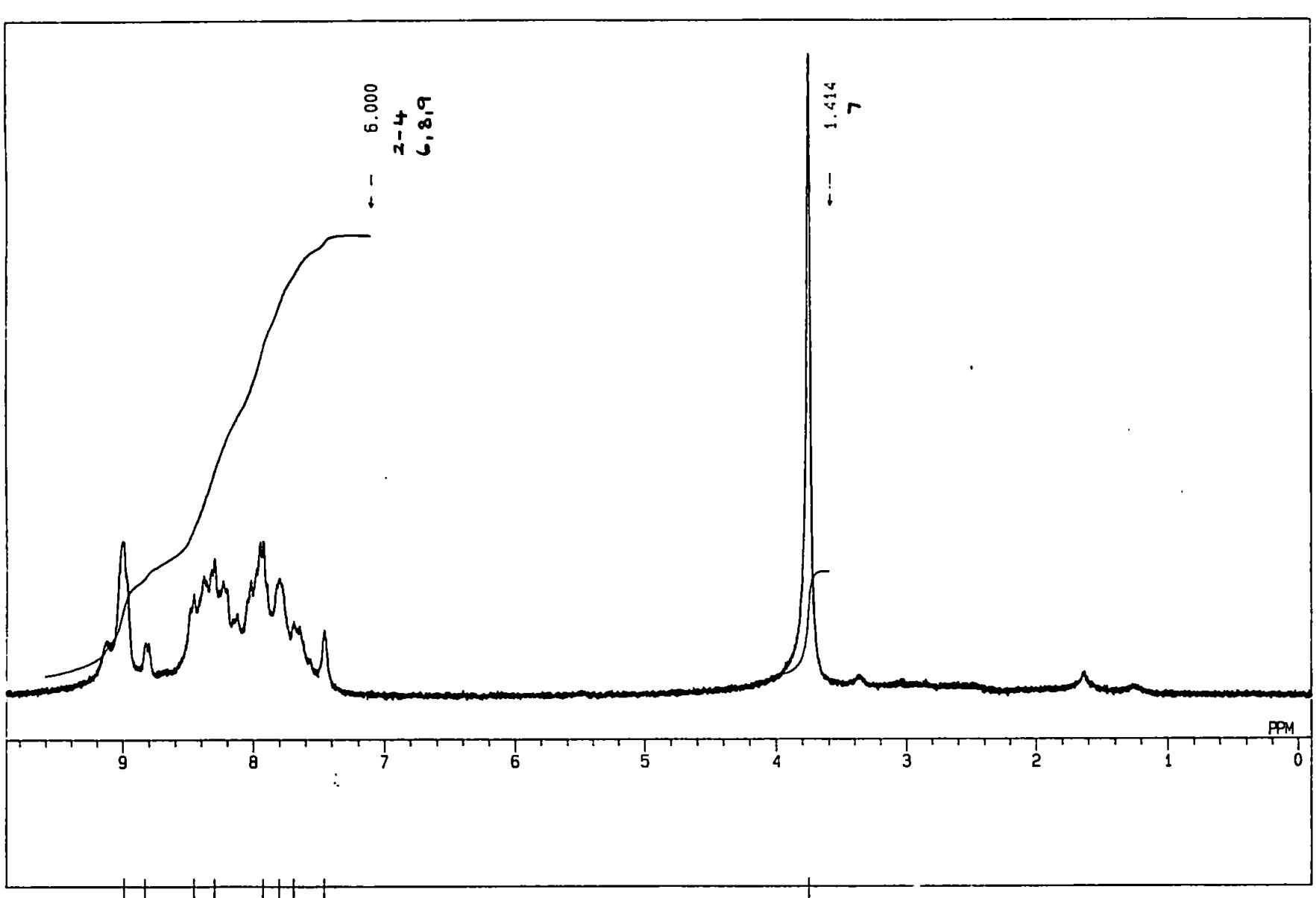


Appendix II.21

7-hydroxy-5H-indeno[1,2-b]pyridin-5-one (242)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.7850	24.13790	2373.42	5445	+++++
2		8.6226	8.31078	2329.54	5578	++
3		8.2489	15.89962	2228.58	5884	+++
4		8.1744	18.64809	2208.46	5945	++++
5		8.0926	21.40289	2186.35	6012	++++
6		8.0267	18.03402	2168.53	6066	++++
7		7.9180	12.97639	2139.17	6155	+++
8		7.8142	18.11195	2111.13	6240	++++
9		7.7421	24.16719	2091.66	6299	+++++
10		7.7214	24.31286	2086.05	6316	+++++
11		7.5968	18.58488	2052.40	6418	++++
12		7.4845	11.89329	2022.05	6510	++
13		7.2500	10.46853	1958.71	6702	++
14	OH-7	3.5462	100.00000	958.06	9735	++++++++++++++++++++



21-APR-93 16: 19: 30

Accumulation

OBNUC 1H
OFR 270.05 MHz
EXMOD NON
POINT 32768
PW1 4.9 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT DMSO

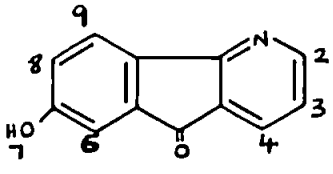
Processing

BF 0.10 Hz
EXREF 2.50 ppm

Plot

XS 198.8348 Hz
XE 2701.6620 Hz
YG 1.98

OPERATOR : _____



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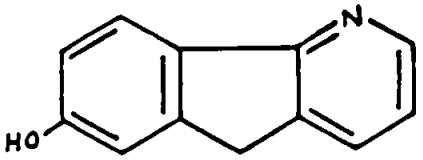
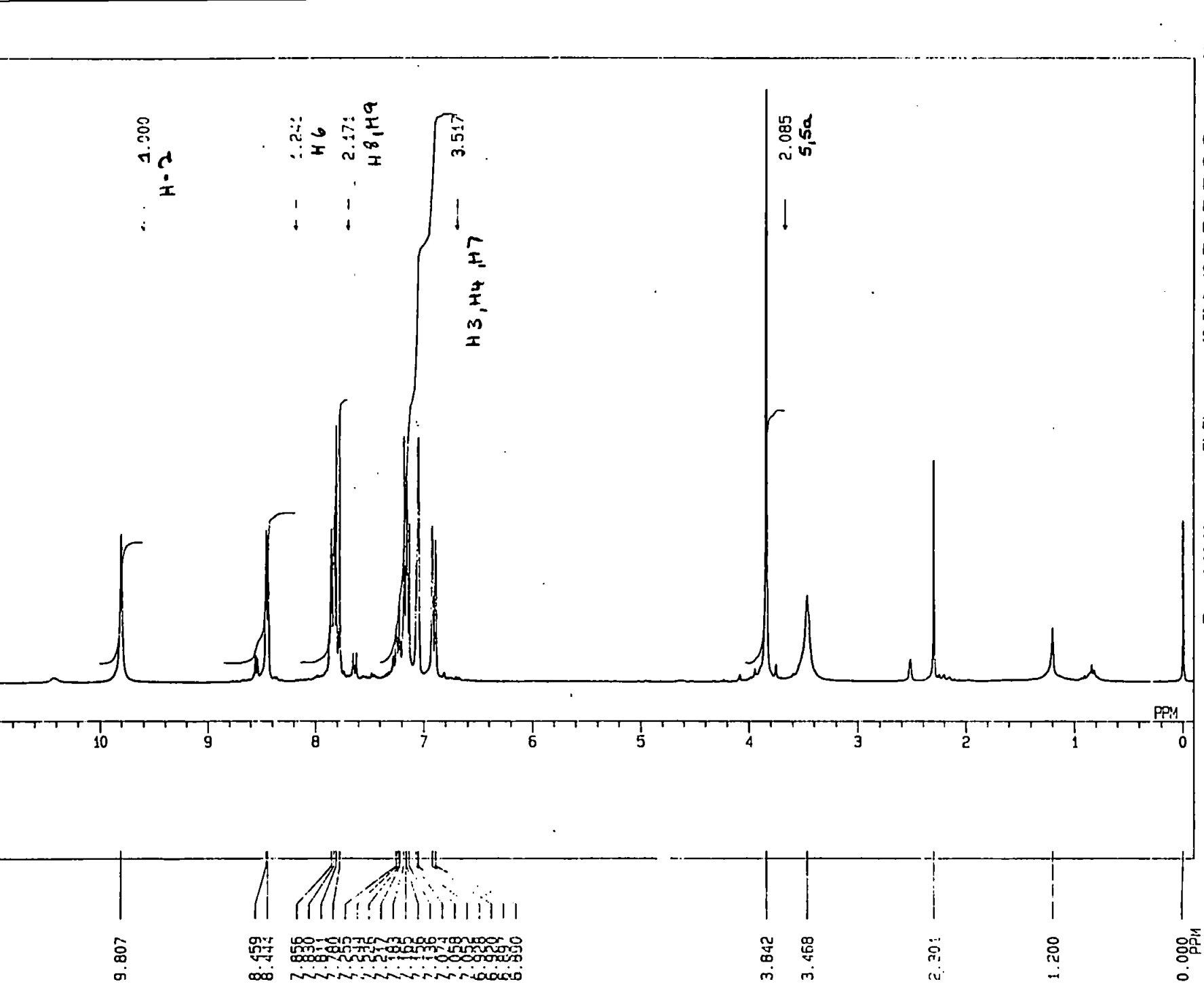
Appendix II.22

7-hydroxy-5H-indeno[1,2-b]pyridine (243)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H2	9.8072	24.90836	2649.59	4453	+++++
2	H6	8.4591	25.50188	2285.35	5557	+++++
3		8.4444	24.51982	2281.40	5569	+++++
4		7.8558	25.77160	2122.37	6051	+++++
5	H8	7.8302	27.80305	2115.45	6072	++++++
6	H9	7.8106	43.30069	2110.17	6088	+++++++++
7		7.7801	45.01842	2101.92	6113	+++++++++
8		7.2550	6.70812	1960.05	6543	++
9		7.2440	7.16210	1957.08	6552	+
10		7.2257	12.31124	1952.14	6567	++
11		7.2171	6.67961	1949.82	6574	+
12	H3	7.1929	41.35785	1940.59	6602	++++++++
13		7.1646	34.83844	1933.64	6617	+++++++
14	H4	7.1561	33.59701	1933.33	6624	+++++++
15	H7	7.1363	26.65825	1928.00	6640	+++++
16		7.0743	19.77472	1911.23	6691	++++
17		7.0584	39.80656	1906.94	6704	++++++++
18		7.0523	41.22701	1905.29	6709	++++++++
19		6.9277	26.21593	1871.63	6811	+++++
20		6.9204	23.80871	1869.66	6817	+++++
21		6.8972	23.86402	1863.39	6836	+++++
22		6.8899	21.46602	1861.41	6842	++++
23	H5,H6G	3.8418	100.00000	1037.93	9338	++++++++++++++++++++
24		3.4681	14.54262	936.97	9644	+++
25		2.3007	37.46760	621.57	10600	+++++++
26		1.2004	9.00425	324.31	11501	++
27		0.0000	27.25309	0.00	12484	+++++



29-APR-93 10:03:27

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

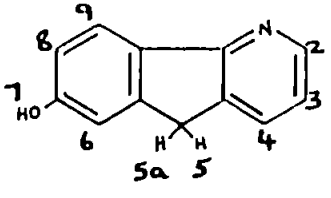
Processing

BF	0.10 Hz
EXREF	0.00 ppm

Plots

XS	-56.3910 Hz
XE	2998.8470 Hz
YG	2.62

OPERATOR : _____



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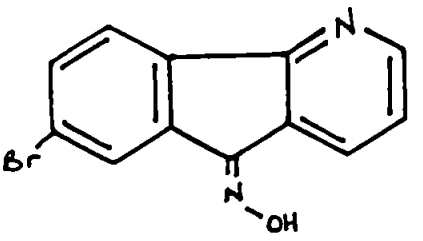
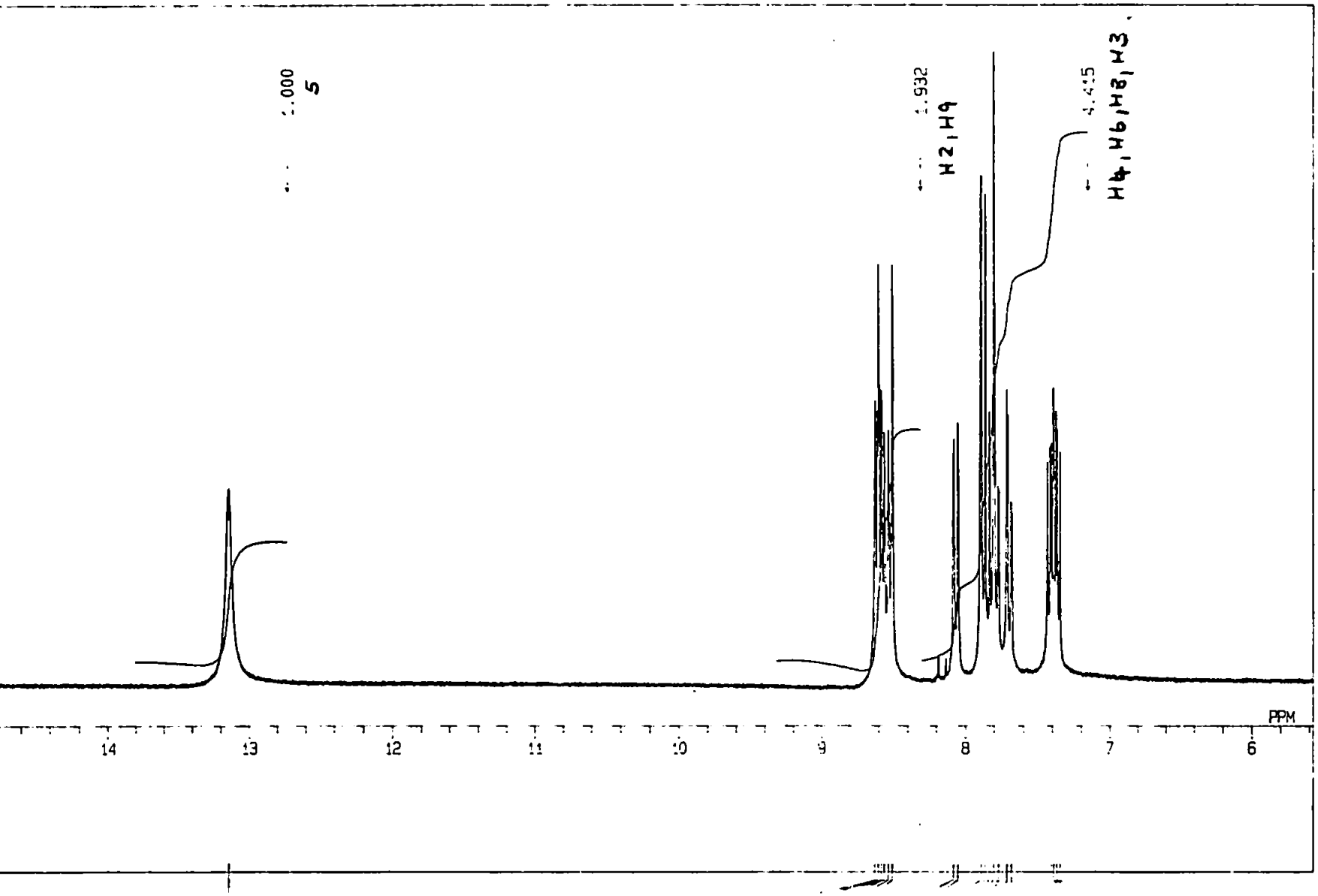
Appendix II.23

7-bromo-5H-indeno[1,2-b]pyridine-5-one oxime (244)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	N-OH	13.1450	30.23531	3551.33	1701	++++++
2		8.6291	34.71949	2331.28	5399	+++++++
3		8.6242	43.87630	2329.96	5403	+++++++++
4		8.6107	42.26242	2326.33	5414	++++++++
5	H2	8.6034	65.07786	2324.35	5420	++++++++++++
6		8.5973	46.34151	2322.71	5425	+++++++++
7	H9	8.5851	45.45659	2319.41	5435	+++++++++
8		8.5790	43.84181	2317.76	5440	+++++++++
9		8.5656	38.97451	2314.13	5451	++++++++
10		8.5595	35.02154	2312.48	5456	+++++++
11		8.5363	39.32384	2306.21	5475	++++++++
12		8.5314	35.57622	2304.89	5479	+++++++
13		8.5106	64.75930	2299.28	5496	++++++++++++
14		8.5045	60.04983	2297.63	5501	++++++++++++
15		8.0844	35.78328	2184.14	5845	+++++++
16		8.0783	37.82746	2182.49	5850	++++++++
17		8.0551	40.46519	2176.22	5869	++++++++
18		8.0502	38.14196	2174.90	5873	++++++++
19		7.8915	78.90148	2132.01	6003	++++++++++++++++
20		7.8634	75.95508	2124.42	6026	++++++++++++++++
21	H4	7.8329	42.13098	2116.18	6051	++++++++
22	H6	7.8036	100.00000	2108.26	6075	++++++++++++++++++++
23		7.7755	30.50197	2100.67	6098	++++++
24	H8	7.7621	29.85196	2098.69	6104	++++++
25	H3	7.7156	45.64473	2084.50	6147	+++++++++
26		7.7095	41.71942	2082.85	6152	++++++++
27		7.6863	28.13245	2076.59	6171	++++++
28		7.6790	26.36101	2074.61	6177	+++++
29		7.4372	34.33937	2009.28	6375	+++++++
30		7.4199	36.66406	2004.33	6390	+++++++
31		7.4091	37.25826	2001.69	6398	+++++++
32		7.3957	45.88066	1998.06	6409	+++++++++
33		7.3938	39.54634	1996.74	6413	++++++++
34		7.3774	42.18675	1993.12	6424	++++++++
35		7.3676	39.41956	1990.48	6432	++++++++
36		7.3493	35.86820	1985.53	6447	+++++++



21-APR-93 15:49:37

Accumulation

OBSCO 1H
OFR 270.05 MHz
EXMOD ND
POINT 32768
PW1 4.9 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT DMSO

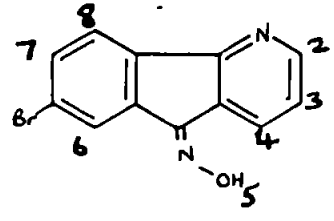
Processing

BF 0.10 Hz
EXREF 2.50 ppm

Plot

XS -1336.8350 Hz
XE 2479.6770 Hz
YG 4.43

OPERATOR : _____



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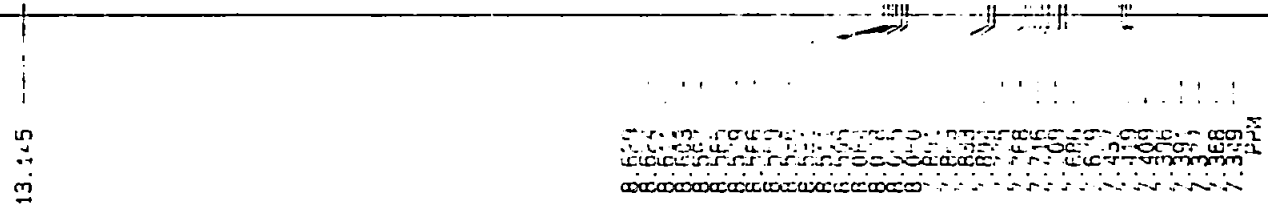
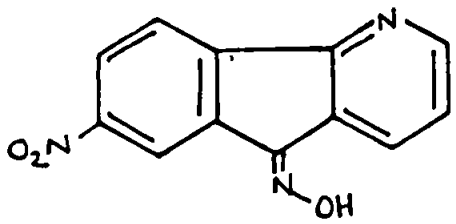
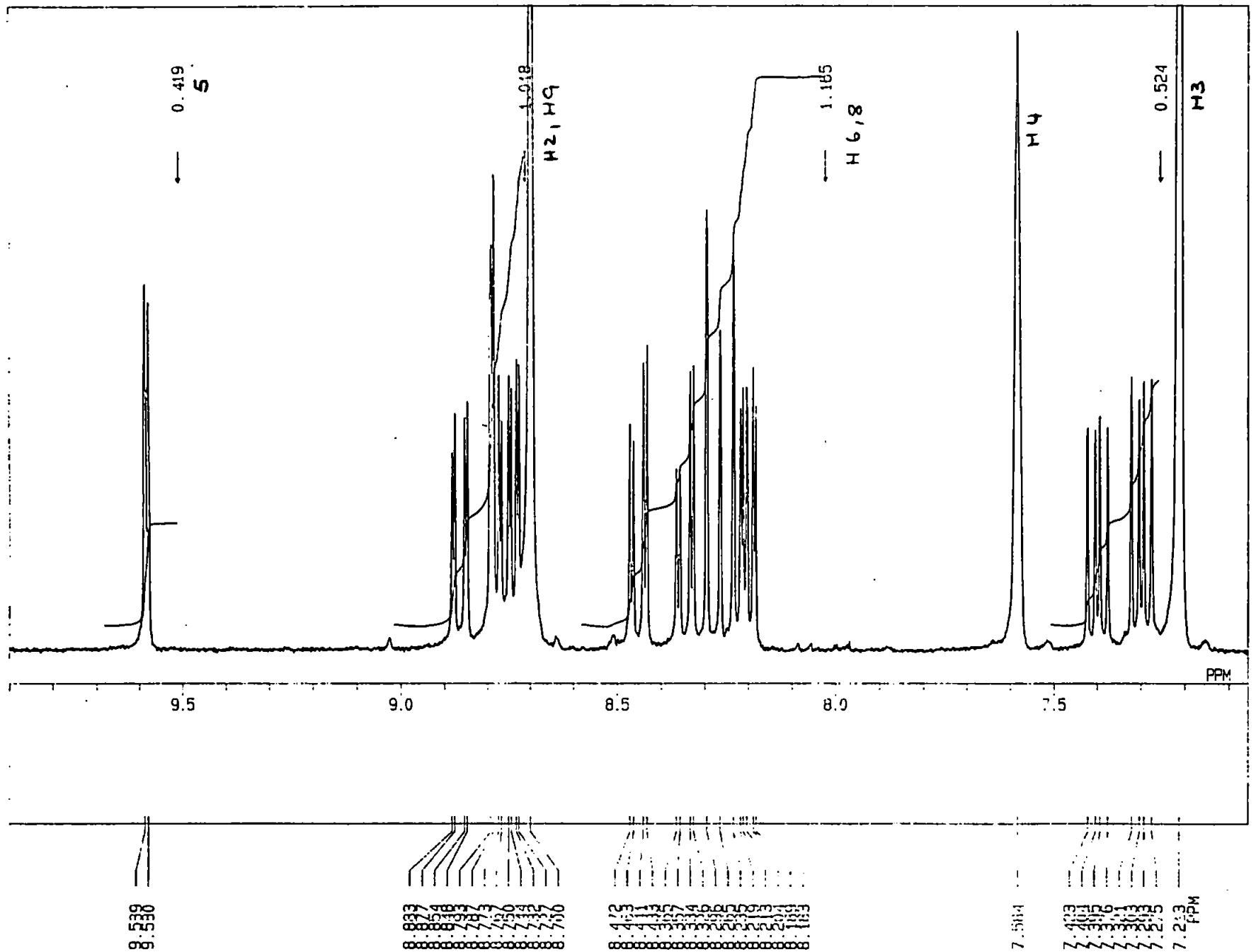


Appendix II.24

7-nitro-5H-indeno[1,2-b]pyridine-5-one oxime (245)



	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
N-OH	9.5890	2.71419	2590.63	4894	+
	9.5605	2.57695	2588.32	4901	+
	8.8832	1.46108	2399.93	5472	
	8.8771	1.74975	2398.29	5477	
	8.8539	1.71994	2392.02	5496	
H2	8.8478	1.84141	2390.37	5501	
H9	8.7928	3.00664	2375.52	5546	+
	8.7867	3.52809	2373.87	5551	+
	8.7733	2.04042	2370.24	5562	
	8.7672	1.69218	2368.59	5567	
	8.7501	2.03471	2363.97	5581	
	8.7440	1.93663	2362.32	5586	
	8.7318	2.15647	2359.02	5596	
	8.7269	2.11516	2357.71	5600	
	8.7000	12.74187	2350.45	5622	+++
	8.4716	1.67040	2288.75	5809	
	8.4631	1.54500	2286.44	5816	
	8.4411	2.12717	2280.50	5834	
	8.4326	2.26039	2278.19	5841	
	8.3654	1.33601	2260.05	5896	
H6	8.3569	1.29231	2257.74	5903	
H8	8.3336	2.06591	2251.47	5922	
	8.3263	2.10950	2249.49	5928	
	8.2958	3.26156	2241.24	5953	+
	8.2653	2.37239	2233.00	5978	
	8.2347	3.05397	2224.75	6003	+
	8.2189	1.78837	2220.46	6016	
	8.2128	1.94247	2218.81	6021	
	8.2042	1.94841	2216.50	6028	
	8.1895	2.09663	2212.54	6040	
	8.1834	1.80230	2210.89	6045	
H4	7.5838	4.58787	2048.90	6536	+
	7.4227	1.64646	2005.35	6668	
	7.4043	1.63347	2000.40	6683	
	7.3946	1.73482	1997.76	6691	
H3	7.3762	1.64754	1992.81	6706	
	7.3213	2.02528	1977.97	6751	
	7.3030	1.85948	1973.02	6766	
	7.2932	1.98931	1970.38	6774	
	7.2749	2.00860	1965.43	6789	
	7.2126	9.85171	1948.60	6840	++



10-MAR-93 10:43:00

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	C5D5N

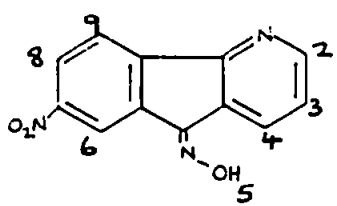
Processing

BF	0.10 Hz
EXREF	8.70 ppm

Plot

XS	-788.2144 Hz
XE	768.4174 Hz
YG	54.87

OPERATOR : _____



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Appendix II. 25

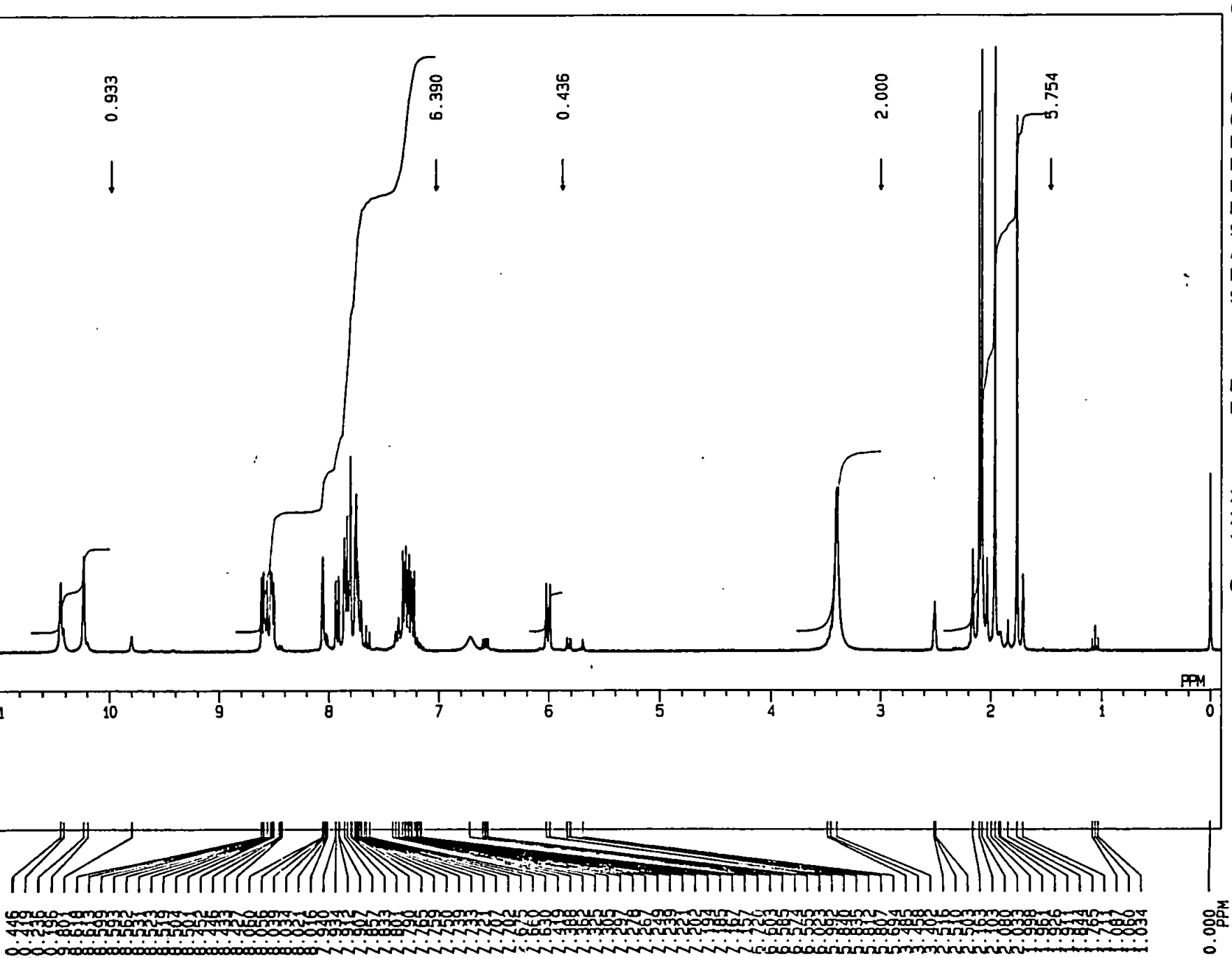
5,7-diacetamido-5H-indeno[1,2-b]pyridine (246)

$C_{16}H_{15}N_3O_2$ (DMSO)

	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	10.4459	11.59951	2822.13	3918	++
2	10.4190	3.95400	2814.88	3940	+
3	10.2359	15.92329	2765.39	4090	+++
4	10.1956	1.52946	2754.50	4123	
5	9.8011	2.67103	2647.94	4446	+
6	8.6178	10.57395	2328.24	5415	++
7	8.6129	12.29016	2326.92	5419	++
8	8.5995	13.02594	2323.29	5430	+++
9	8.5934	13.30185	2321.65	5435	+++
10	8.5616	11.65209	2313.07	5461	++
11	8.5311	13.42087	2304.82	5486	+++
12	8.5226	13.09153	2302.51	5493	+++
13	8.5189	12.90824	2301.52	5496	+++
14	8.5042	11.48461	2297.56	5508	++
15	8.5006	11.14984	2296.57	5511	++
16	8.4517	0.88422	2283.37	5551	
17	8.4456	0.98331	2281.73	5556	
18	8.4334	0.83217	2278.43	5566	
19	8.4273	0.87579	2276.78	5571	
20	8.0597	14.82575	2177.47	5872	+++
21	8.0561	15.76202	2176.48	5875	+++
22	8.0390	2.88997	2171.86	5889	+
23	8.0341	2.97926	2170.54	5893	+
24	8.0207	2.75195	2166.91	5904	+
25	8.0158	2.73011	2165.59	5908	+
26	7.9401	11.34477	2145.14	5970	++
27	7.9340	11.74506	2143.49	5975	++
28	7.9120	12.47721	2137.55	5993	++
29	7.9071	11.63077	2136.23	5997	++
30	7.8570	18.93273	2122.70	6038	++++
31	7.8326	22.42638	2116.11	6058	++++
32	7.8008	30.37105	2107.53	6084	++++++
33	7.7899	5.37771	2104.56	6093	+
34	7.7654	18.80062	2097.96	6113	++++
35	7.7593	20.93548	2096.31	6118	++++
36	7.7496	26.05256	2093.67	6126	+++++
37	7.7386	14.89077	2090.70	6135	+++
38	7.7325	13.12730	2089.05	6140	+++
39	7.7215	6.44435	2086.08	6149	+
40	7.7068	8.38797	2082.12	6161	++
41	7.7019	7.25811	2080.80	6165	+
42	7.6751	1.21578	2073.55	6187	
43	7.6604	4.22485	2069.59	6199	+
44	7.6299	3.20869	2061.34	6224	+
45	7.4186	0.87473	2004.26	6397	
46	7.3881	3.29474	1996.01	6422	+
47	7.3624	5.50129	1989.09	6443	+
48	7.3246	16.71352	1978.86	6474	+++
49	7.3051	14.83820	1973.58	6490	+++
50	7.2965	17.52430	1971.27	6497	++++
51	7.2782	13.56267	1966.32	6512	+++
52	7.2672	16.07304	1963.35	6521	+++
53	7.2489	13.29687	1958.40	6536	+++
54	7.2391	12.04905	1955.76	6544	++
55	7.2208	13.38112	1950.82	6559	+++

Appendix II.25 (cont'd)

56	7.2025	1.36145	1945.87	6574	
57	7.1939	2.23707	1943.56	6581	
58	7.1854	1.36961	1941.25	6588	
59	7.1671	1.32198	1936.30	6603	
60	7.1573	0.85904	1933.66	6611	
61	6.7201	2.40479	1815.55	6969	
62	6.6029	1.97881	1783.88	7065	
63	6.5846	1.92995	1778.93	7080	
64	6.5736	2.06444	1775.96	7089	
65	6.5553	2.09167	1771.01	7104	
66	6.0228	11.23048	1627.16	7540	++
67	5.9923	11.04130	1618.92	7565	++
68	5.8396	2.10939	1577.68	7690	
69	5.8348	2.24826	1576.36	7694	
70	5.8116	2.03620	1570.09	7713	
71	5.8067	2.00861	1568.77	7717	
72	5.6943	1.87254	1538.42	7809	
73	3.4852	1.91471	941.59	9618	
74	3.4584	4.01632	934.33	9640	+
75	3.4022	27.06349	919.16	9686	+++++
76	2.5156	5.98849	679.63	10412	+
77	2.5095	8.09927	677.99	10417	++
78	2.5034	5.90755	676.34	10422	+
79	2.1627	16.91301	584.29	10701	+++
80	2.1029	87.46676	568.12	10750	++++++++++++++++++
81	2.0797	99.59109	561.85	10769	++++++++++++++++++++
82	2.0333	15.43306	549.32	10807	+++
83	1.9978	2.10620	539.75	10836	
84	1.9612	100.00000	529.85	10866	++++++++++++++++++++++
85	1.9258	2.99309	520.28	10895	+
86	1.9111	3.12926	516.32	10907	+
87	1.8440	5.09319	498.18	10962	+
88	1.7646	88.73619	476.73	11027	++++++++++++++++++
89	1.7109	12.75955	462.22	11071	+++
90	1.0868	1.95192	293.63	11582	
91	1.0600	4.10774	286.37	11604	+
92	1.0343	2.09563	279.44	11625	
93	0.0000	29.37670	0.00	12472	+++++



05-MAY-93 14: 12: 30

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

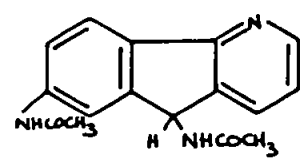
Processing

BF	0.10 Hz
EXREF	0.00 ppm

Plot

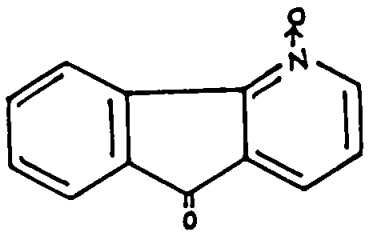
XS	-60.3500 Hz
XE	2998.8470 Hz
YG	3.20

OPERATOR : _____

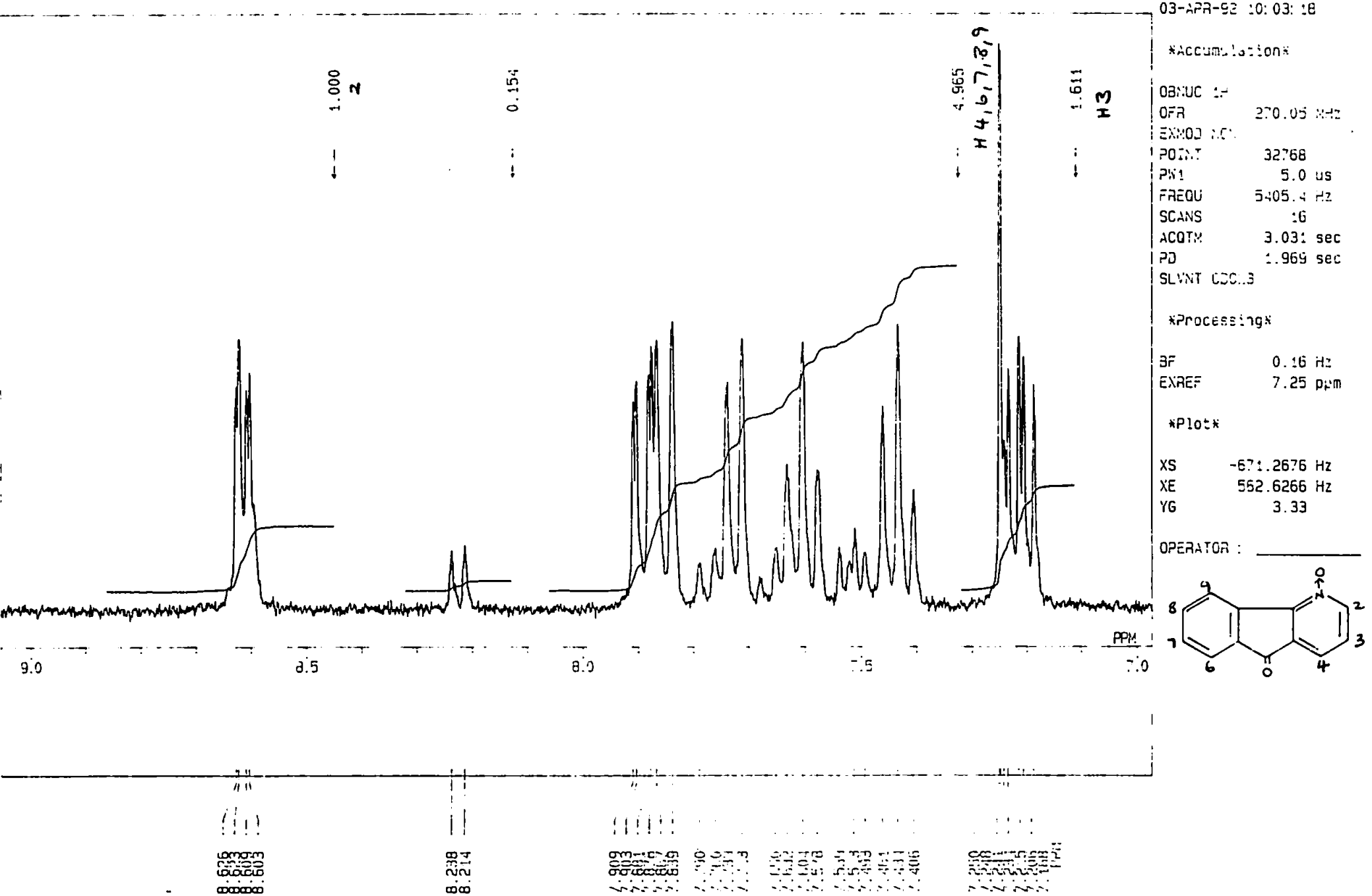


Appendix II.26

5H-indeno[1,2-b]pyridine-5-one N-oxide (249)



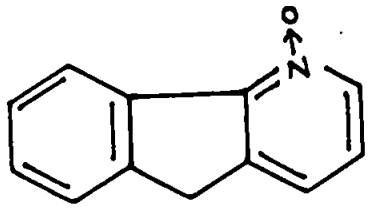
PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
8.6263	39.44349	2330.53	5657	++++++++
8.6226	47.91145	2329.54	5660	++++++++++
8.6092	38.81522	2325.91	5671	++++++++
8.6031	41.84488	2324.26	5676	++++++++
8.2379	10.18593	2225.61	5975	++
8.2135	11.09416	2219.01	5995	++
7.9094	36.62215	2136.86	6244	+++++++
7.9033	40.23669	2135.21	6249	++++++++
7.8813	41.40897	2129.27	6267	++++++++
7.8777	46.46135	2128.28	6270	+++++++++
7.8667	47.49572	2125.31	6279	+++++++++
7.8366	50.88221	2117.73	6302	++++++++++
7.7896	8.05587	2104.53	6342	++
7.7605	10.60693	2096.61	6366	++
7.7385	40.16207	2090.67	6384	++++++++
7.7125	47.96439	2083.75	6405	++++++++++
7.6505	10.75589	2066.92	6456	++
7.6322	25.59409	2061.97	6471	+++++
7.6041	47.31322	2054.38	6494	+++++++++
7.5785	24.55281	2047.45	6515	+++++
7.5394	10.80749	2036.90	6547	++
7.5126	14.26042	2029.64	6569	+++
7.4930	9.82348	2024.36	6585	++
7.4613	35.81815	2015.78	6611	+++++++
7.4344	50.36570	2008.52	6633	++++++++++
7.4063	21.01907	2000.94	6656	++++
7.2500	100.00000	1958.71	6784	++++++++++++++++++++
7.2476	98.76773	1958.05	6786	++++++++++++++++++++
7.2415	29.75432	1956.40	6791	++++++
7.2341	42.43372	1954.42	6797	++++++++
7.2146	48.33008	1949.14	6813	++++++++++
7.2060	44.59966	1946.83	6820	+++++++++
7.1877	39.70894	1941.88	6835	++++++++


03-APR-92 10:03:18
Accumulation
OBNUC 1H
OFR 270.05 MHz
EXMOD NONE
POINT 32768
PW1 5.0 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT CDCL3
Processing
BF 0.16 Hz
EXREF 7.25 ppm
Plot
XS -671.2676 Hz
XE 562.6266 Hz
YG 3.33
OPERATOR :
1.000
2
0.154
4.965
H 4,6,7,8,9
1.611
H3
PPM
9.0
8.5
8.0
7.5
7.0
8.635
8.633
8.609
8.603
8.238
8.214
7.909
7.903
7.406

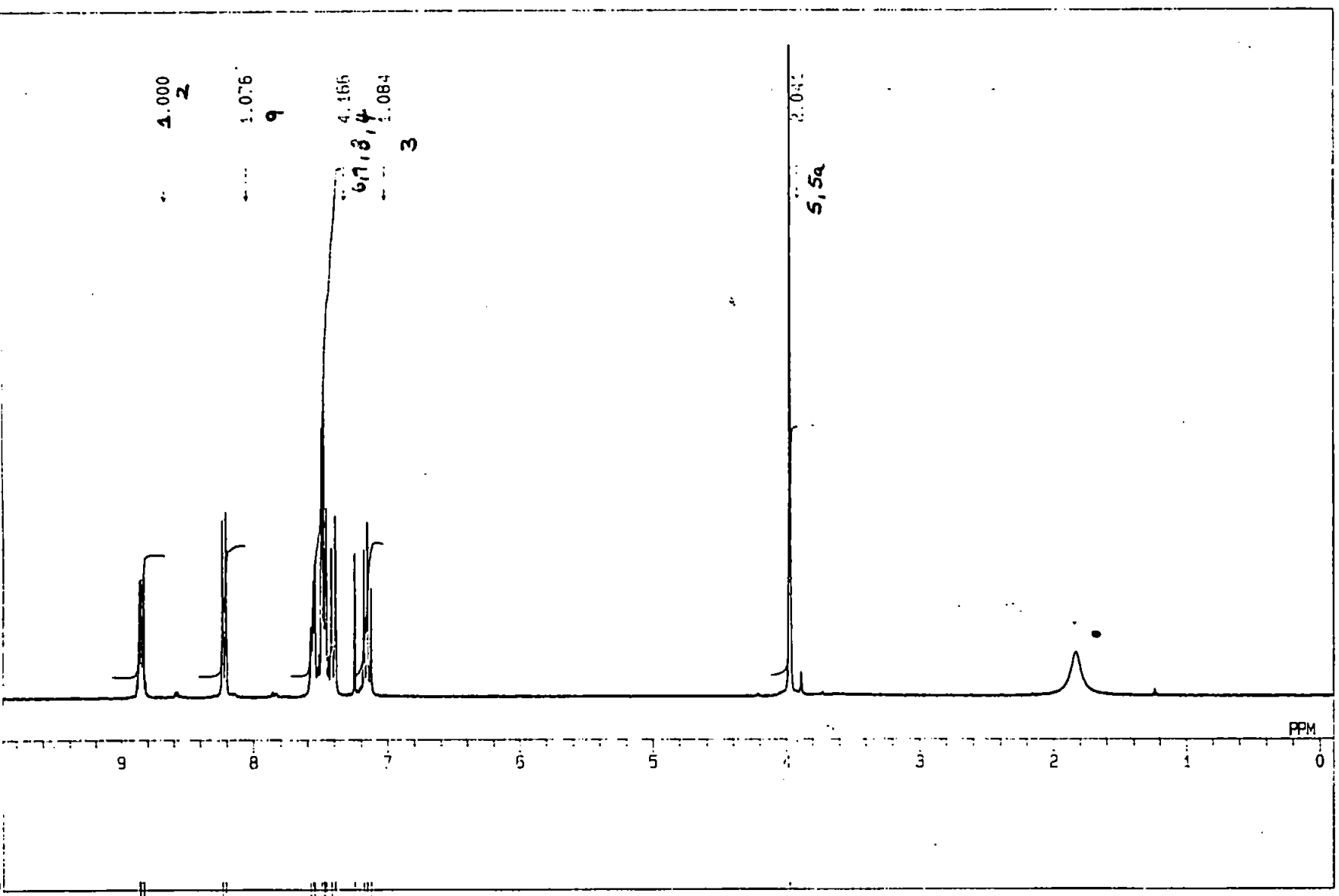
337

Appendix II.27

5H-indeno[1,2-b]pyridine N-oxide (250)



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1		8.8656	17.94974	2395.19	5462	++++
2		8.8558	15.95532	2392.55	5470	+++
3	H-2	8.8510	18.15973	2391.23	5474	++++
4		8.8387	12.54087	2387.93	5484	+++
5		8.8326	18.41249	2386.28	5489	++++
6	H-9	8.2343	27.16943	2224.62	5979	+++++
7		8.2098	28.43790	2218.02	5999	++++++
8		7.5748	10.60066	2046.46	6519	++
9		7.5577	17.68717	2041.85	6533	++++
10		7.5443	19.72029	2038.22	6544	++++
11	H6	7.4913	41.30140	2024.03	6587	+++++++++
12	H7	7.4771	48.43285	2020.07	6599	++++++++++
13	H8	7.4674	22.72690	2017.43	6607	+++++
14	H4	7.4600	28.99748	2015.45	6613	++++++
15		7.4210	22.91926	2004.89	6645	+++++
16		7.3929	27.90223	1997.31	6668	++++++
17		7.2500	21.95946	1958.71	6785	++++
18		7.1816	22.64853	1940.23	6841	+++++
19	H3	7.1572	26.95849	1933.63	6861	+++++
20		7.1291	16.61345	1926.04	6884	+++
21	H5,5a	3.9736	100.00000	1073.53	9468	++++++++++++++++++++



21-APR-93 15:27:35

Accumulation

OBNUC 1H
OFR 270.05 MHz
EXMOD NONE
POINT 32768
PW1 4.9 us
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 1.969 sec
SLVNT CDCL3

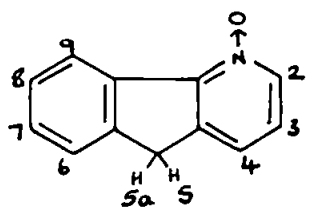
Processing

BF 0.10 Hz
EXREF 7.25 ppm

Plot

XS 170.6935 Hz
XE 2701.6630 Hz
YG 3.36

OPERATOR : _____



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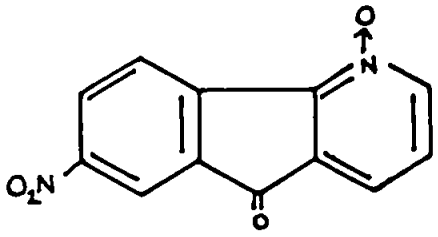
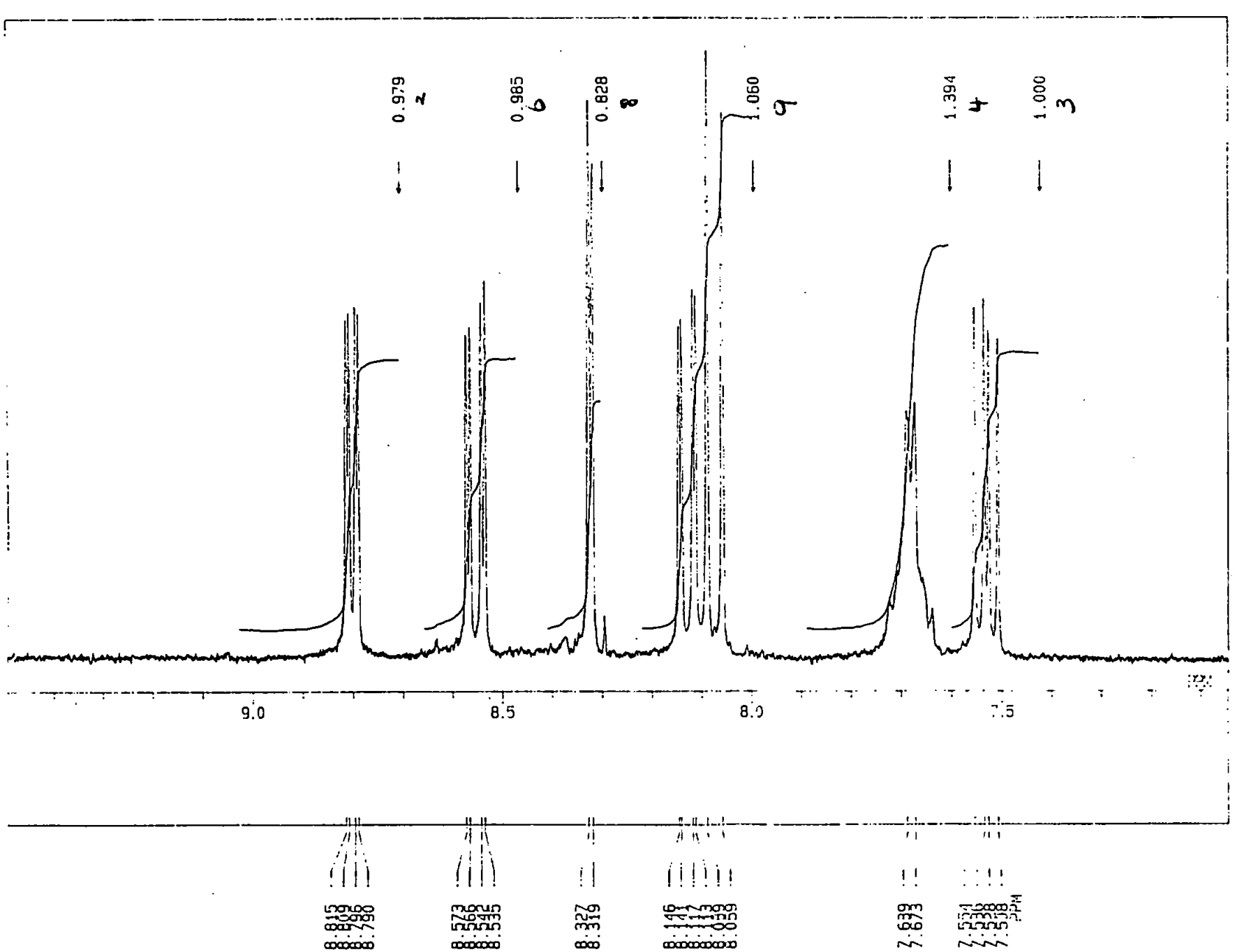
Appendix II.28

7-nitro-5H-indeno[1,2-b]pyridine-5-one N-oxide (251).



NO.		PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	H-2	8.8147	0.34534	2381.43	5246	
2		8.8086	0.35291	2379.78	5251	
3		8.7964	0.35973	2376.48	5261	
4		8.7903	0.35182	2374.83	5266	
5	H-6	8.5729	0.33058	2316.11	5444	
6		8.5656	0.33848	2314.13	5450	
7		8.5424	0.36372	2307.86	5469	
8		8.5350	0.38600	2305.88	5475	
9	H-8	8.3274	0.57210	2249.79	5645	
10		8.3189	0.50723	2247.48	5652	
11	H-9	8.1455	0.33829	2200.64	5794	
12		8.1406	0.34581	2199.32	5798	
13		8.1174	0.37629	2193.05	5817	
14		8.1125	0.36977	2191.73	5821	
15		8.0893	0.62188	2185.46	5840	
16		8.0583	0.55894	2177.21	5865	
17	H-4	7.6888	0.25098	2077.25	6168	
18		7.6729	0.25972	2072.96	6181	
19	H-3	7.5544	0.35756	2040.95	6278	
20		7.5361	0.36662	2036.01	6293	
21		7.5276	0.33418	2033.70	6300	
22		7.5080	0.32642	2028.42	6316	
23		3.5014	1.59367	945.95	9597	
24		3.4501	100.00000	932.09	9639	++++++++++++++++++++
25		3.4012	1.26684	918.90	9679	
26		3.3560	0.19154	906.69	9716	
27		2.5379	0.29589	685.64	10386	
28		2.5122	1.18327	678.72	10407	
29		2.5061	2.39991	677.07	10412	
30		2.4988	3.21457	675.09	10418	+
31		2.4927	2.29577	673.44	10423	
32		2.4853	1.01316	671.46	10429	
33		1.8711	0.27448	505.51	10932	
34		1.2104	0.32770	327.02	11473	
35		0.8722	0.25104	235.63	11750	
36		0.8392	0.66981	226.73	11777	
37		0.8148	0.63776	220.13	11797	
38		0.7855	0.42686	212.21	11821	
39		0.7586	0.27728	204.95	11843	



02-FEB-93 10:28:37

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	DMSO

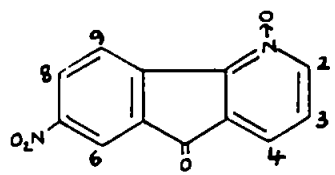
Processing

BF	0.10 Hz
EXREF	2.50 ppm

Plot

XS	-824.7994 Hz
XE	661.1592 Hz
YG	385.33

OPERATOR : _____



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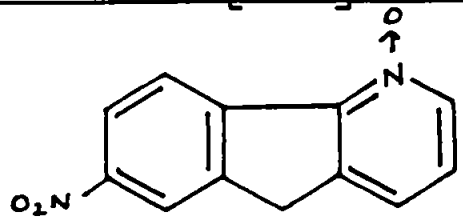
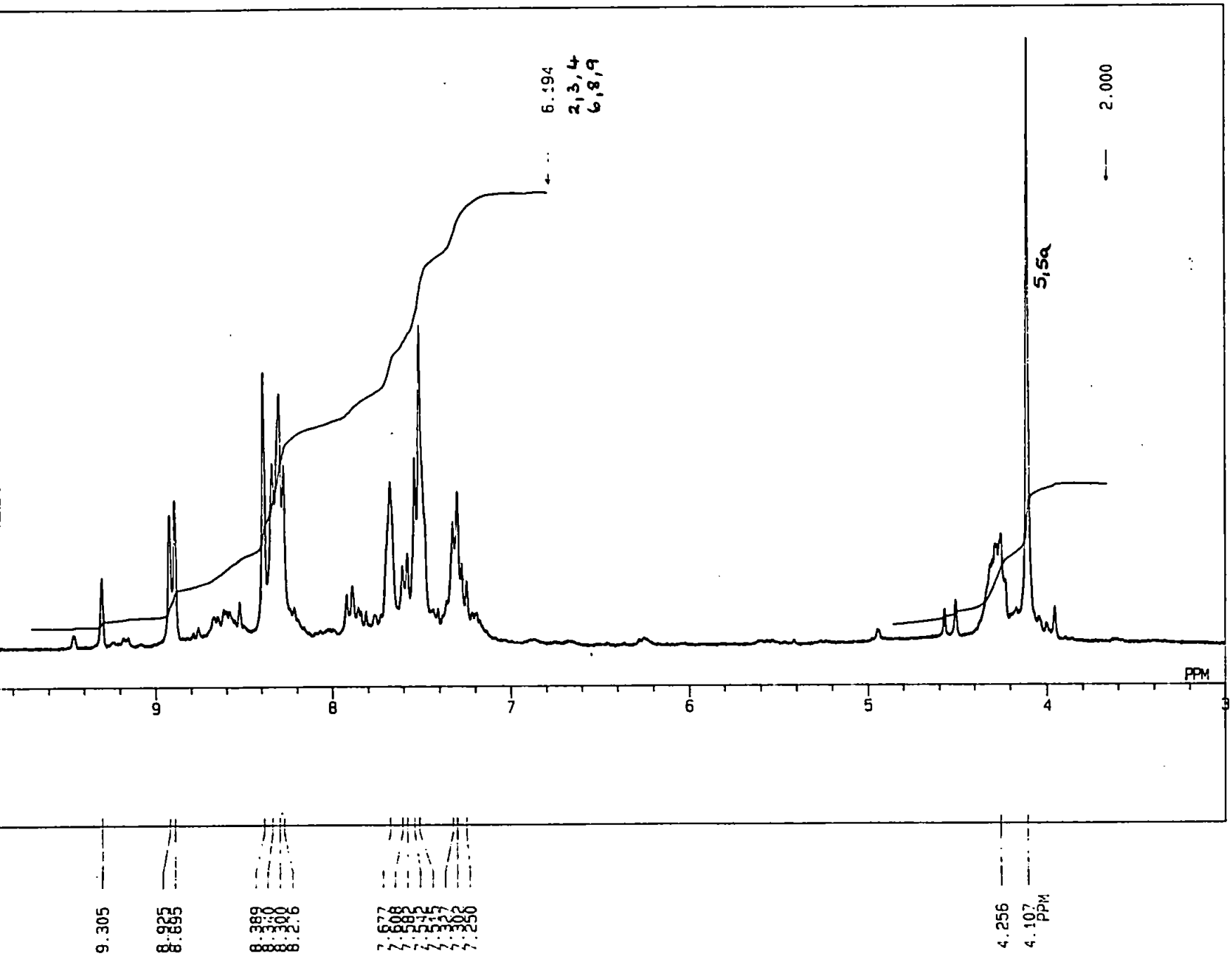
Appendix II.29

7-nitro-5H-indeno[1,2-b]pyridine N-oxide (252)



NO.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	9.3052	11.02399	2513.96	5101	++
2	8.9254	21.54550	2411.36	5412	++++
3	8.8949	24.01931	2403.11	5437	+++++
4	8.3894	45.24946	2266.52	5851	+++++++++
5	8.3405	29.95539	2253.32	5891	++++++
6	8.3002	41.68136	2242.44	5924	++++++++
7	8.2758	29.60346	2235.84	5944	++++++
8	7.6774	26.84201	2074.18	6434	+++++
9	7.6078	12.89547	2055.37	6491	+++
10	7.5822	14.88324	2048.44	6512	+++
11	7.5419	30.75422	2037.56	6545	++++++
12	7.5150	52.84500	2030.30	6567	++++++++++
13	7.3269	20.18657	1979.49	6721	++++
14	7.3025	23.08932	1972.89	6741	+++++
15	7.2900	10.28027	1958.71	6784	++
16	4.2557	17.77411	1149.74	9236	++++
17	4.1067	100.00000	1109.49	9358	++++++++++++++++++++



29-APR-93 11:49:19

Accumulation

OBNUC	1H
OFR	270.05 MHz
EXMOD	NON
POINT	32768
PW1	4.9 us
FREQU	5405.4 Hz
SCANS	16
ACQTM	3.031 sec
PD	1.969 sec
SLVNT	CDCL3

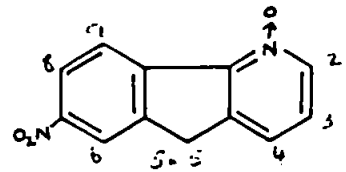
Processing

BF	0.10 Hz
EXREF	7.25 ppm

Plot

XS	-248.3940 Hz
XE	1864.1470 Hz
YG	8.70

OPERATOR : _____



Appendix III

13-C nmr.

Summary of ^{13}C NMR (appendix III)

^{13}C NMR studies have been undertaken by Formichov et al[113] and Wentrup and Mayer[71] for three of the four isomeric indenopyridines. Their results for 5H-indeno[1,2-b]pyridine (4) are shown in Table 8.

Table 8. ^{13}C NMR 5H-indeno 1,2-b pyridine

Attribution Carbon No	$\delta^{13}C$ ppm	Expected Shift ppm	$\Delta\delta$ Eu(dpm)$_3$
9b	158.9	159.0	4.64
2	146.9	146.4	10.60
5a	142.5	143.0	1.55
9a	139.9	138-141.0	2.00
4a	135.7	136.0	-0.44
4	130.8	131-133	2.40
7/8	127.5	126-128	0.70
7/8	125.9	126-128	0.70
6(3)	124.0	124.8	0.70
9	119.8	119.7	4.00
3(6)	119.8	119-121	2.00
5	33.6	37	1.30

In general ^{13}C NMR was used to confirm the structure of the indenopyridine, ie the correct number of carbon atoms were present. In some cases attempts have been made to assign values to the carbon atoms by comparison with the reference compound (4) shown above.

Appendix III.1 shows the spectra for (4).All the values correspond very closely except for that of C-5 which in this case was found to be slightly upfield from the quoted value , at δ =34.377 ppm (Ref δ =37ppm).

Appendix III.2 shows the spectra of the oxo compound (8). The values are similar to that of the methylene compound except for C-5, whose chemical shift is δ= 192 ppm.

The spectra for the carboxylic acid (appendix III.3), (158) shows only 10 peaks. This must mean that 2 pairs of carbon atoms must be equivalent.The COOH carbon is found ,as expected[114] , at δ = 169ppm.

For the hydrazone (55), appendix III.4 , the chemical shift is at δ = 157.7

For the alcohols (215) and (222) the chemical shifts of C-5 are found at 71.729 and 80.829 ppm (appendix III.5 and 6).

For the oximes (224),(225) and (226), the C-5 has a chemical shift of δ =150.8 ppm (appendix III.7,8,9). Appendix III.8 and 9 also show chemical shifts for CH_2 at 76.9 and 74.4 ppm respectively.

The chemical shift for C=O of the acetamide group in compound (230), appendix III.10 , is found at δ =170.7ppm The methyl carbon has a chemical shift of δ = 53.007 ppm.

The NMR spectra for the bromo compound (233) is shown in appendix III.11 and has a chemical shift, for C-5 , of δ =190 ppm. The C-7 carbon may have a chemical shift of δ = 127 ppm.

Similarly, for the dibromo compound (234), the chemical shift for C-7 and C-9 carbons maybe 134.4 and 127.45 ppm, respectively. Appendix III.12

Appendix III.13 shows the spectra of the tetrabromo compound (237).Only nine peaks are seen,indicating that some of the carbons must be equivalent.
To find out whether the bromine atoms are on the C6-C9 carbon or at the methylene position a DEPT measurement was carried out.A positive peak indicates a CH carbon atom and a negative peak indicates a CH_2 carbon. In this case, appendix III.15 , three positive peaks are seen and one negative peak at 37.282. This proves that the bromine atoms are substituting at the C6,7,8 and 9 position and not at the methylene position.

For the nitro compound (238),appendix III.15 indicates a chemical shift for C-5 at δ=188.9 ppm.The chemical shift of C-7 maybe at δ=135.5 ppm, by comparison with the spectra for (8).
Appendix III.16 shows the spectra for the reduced nitro compound (239).The spectra indicates the presence of three isomers with CH_2 resonances appearing at δ=34.8 , 34.7 and 34.5 ppm.This indicates that nitration maybe occuring at C-6 and C-9 position as well as the expected C-7 position to give the three nitro- isomers that are seen.

The amino compound ,whose spectra is shown in appendix III.17 has a chemical shift for C-5 at δ=192 ppm.
The chemical shift of C-7 maybe at δ=136.3 ppm, by comparison with the spectra for (8).
The spectra for the N-oxide of (8), appendix III.18 , was very similar to that for (8).

In general, the chemical shifts for the carbon atoms of the pyridyl ring do not alter very much.The values for the benzene carbons are also very similar.

Only does the value of C-5 alter; in the oxo compounds the chemical shift is approximately δ= 192 ppm. For the oximes , hydrazone and acetamide compounds the shift is reduced to δ=151,157 and 159 ppm respectively.

When an alcohol group is attached to C-5,the chemical shift is reduced further to δ=70 or 80ppm.

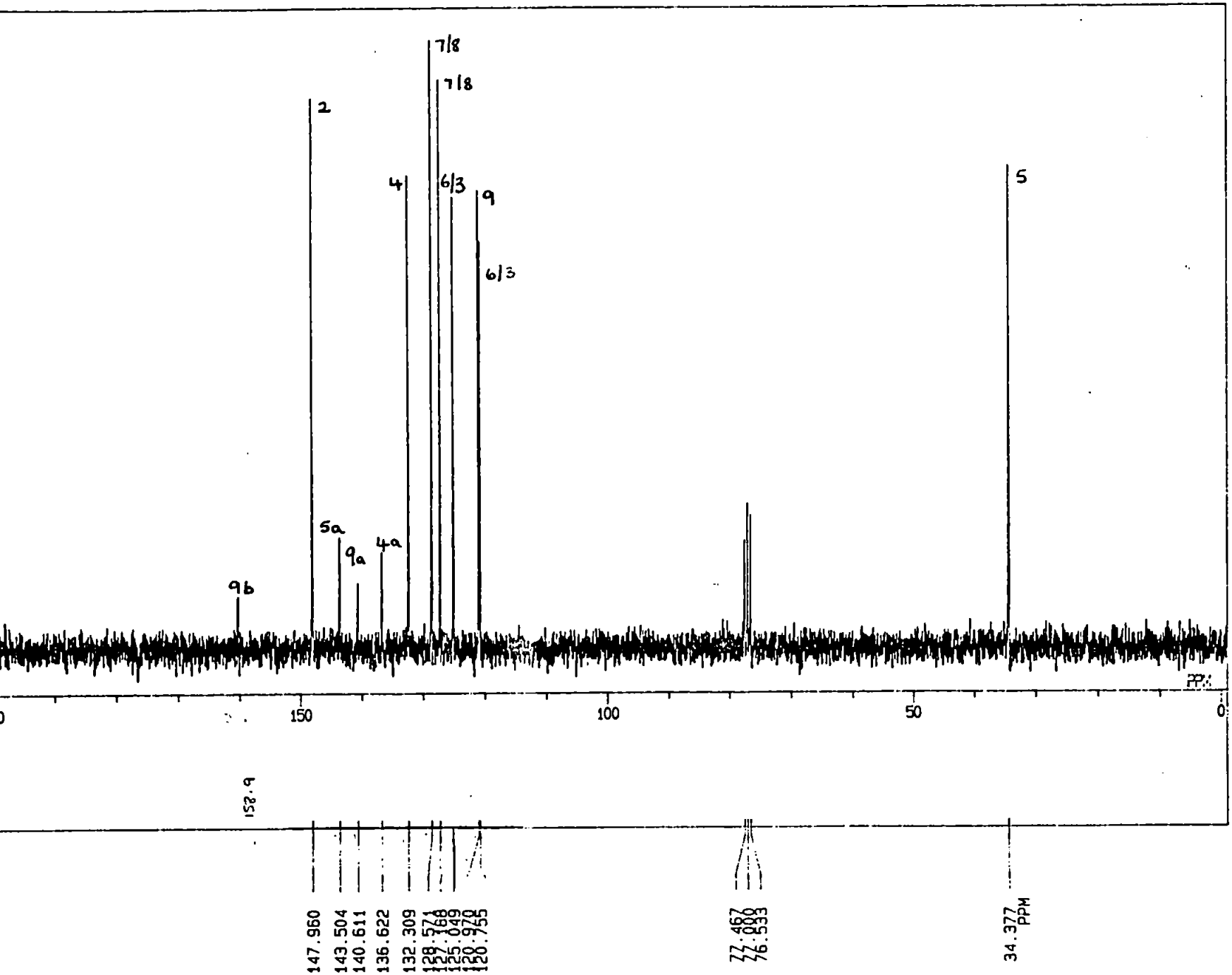
For the methylene compounds , the chemical shift is approximately δ=37 ppm.

Appendix III.1

5H-indeno[1,2-b]pyridine (4)

$C_{12}H_9NO$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
	160.100		
1	147.960	90.54817	10051.4
2	143.504	17.88136	9748.7
3	140.611	10.34391	9552.2
4	136.622	15.39841	9281.2
5	132.309	77.80962	8988.2
6	128.571	100.00000	8734.3
7	127.188	93.59549	8640.3
8	125.049	74.08118	8495.0
9	120.970	75.18009	8217.9
10	120.755	66.70911	8203.3
11	34.377	79.12939	2335.4



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PD	1.181 sec
SLVNT	CDCL3

Processing

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EXREF	77.00 ppm

Plot

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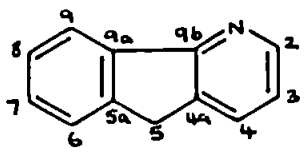
YG	2.47

OPERATOR : _____



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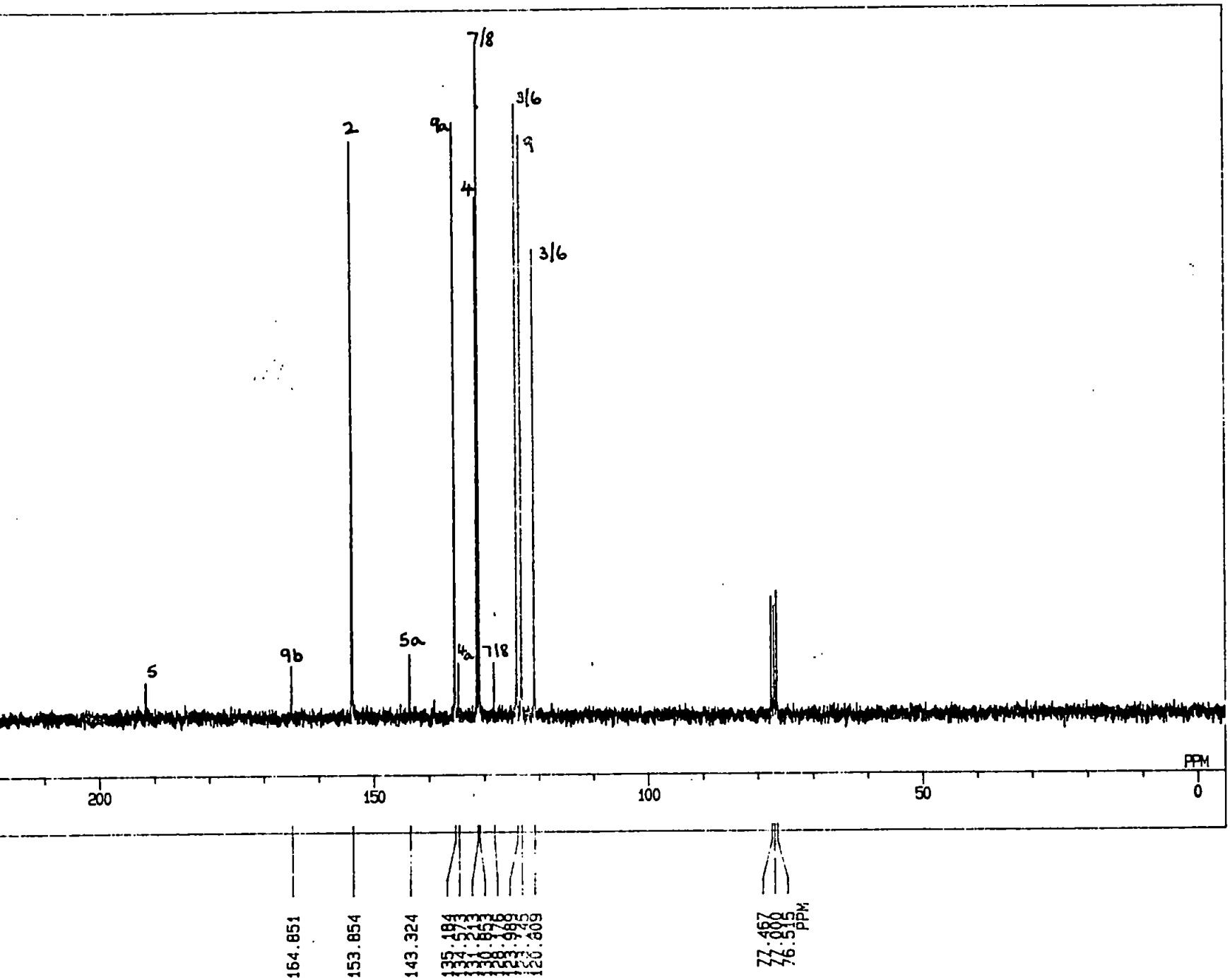
Appendix III.2

5H-indeno[1,2-b]pyridine-5-one (*8*)

$C_{12}H_7NO$ ($CDCL_3$)

No	PPM	INT(%)	FREQ(Hz)
.	192.000		
1	164.851	7.69008	11198.9
2	153.854	86.04605	10451.8
3	143.324	9.32347	9736.5
4	135.184	88.77431	9183.5
5	134.573	7.98209	9142.0
6	131.213	77.45042	8913.7
7	130.853	100.00000	8889.3
8	128.176	7.98091	8707.4
9	123.989	91.44891	8423.0
10	123.145	86.86009	8365.6
11	120.809	69.70526	8206.9



EX270

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SLVNT	CDCL3

Processing

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Plot

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YG	1.93

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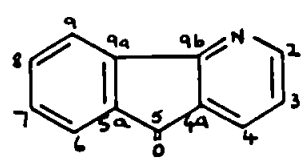

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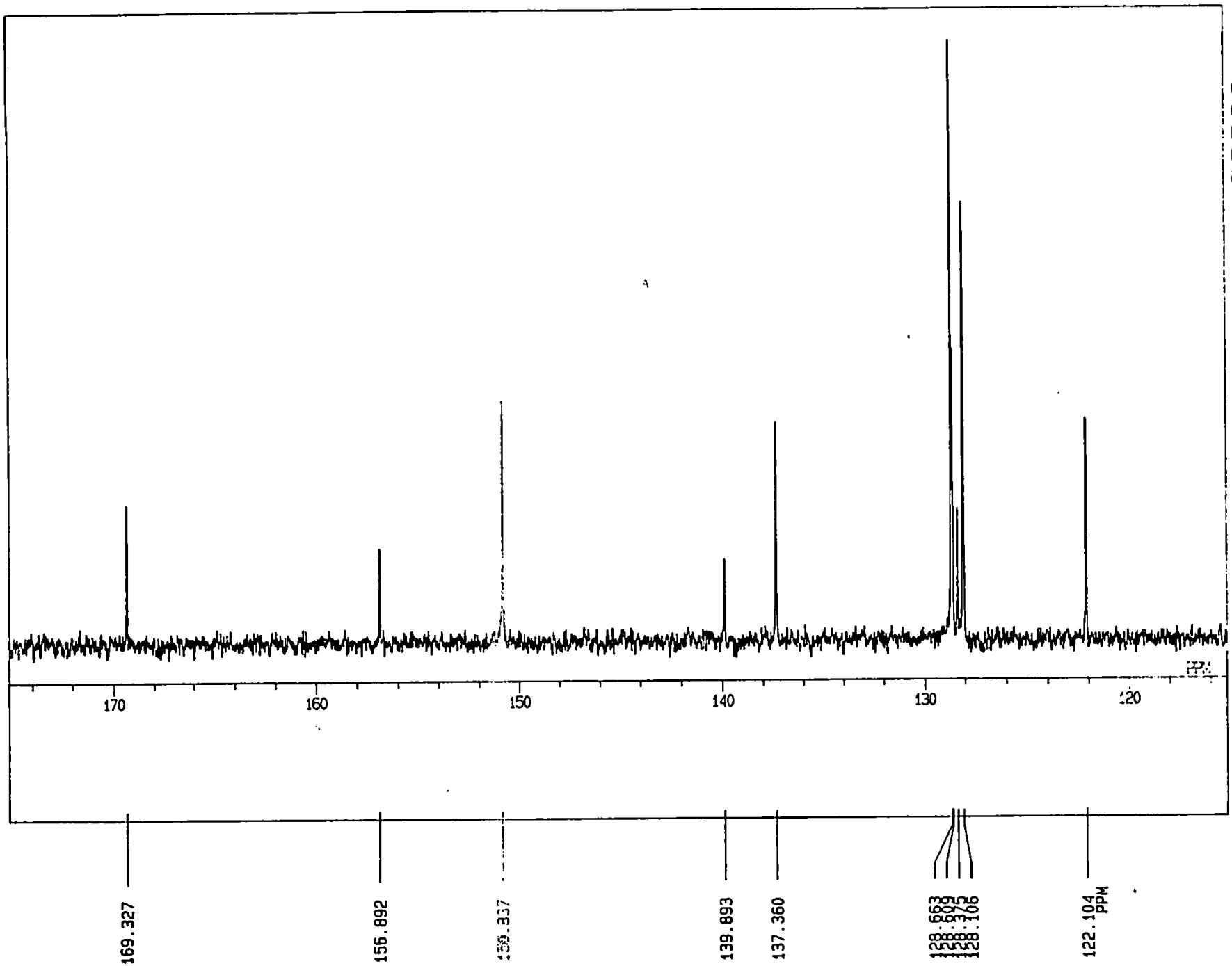
Appendix III.3

2-phenyl-3-pyridine carboxylic acid (158)

$C_{12}H_9NO_2$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	169.327	23.20372	11503.0
2	156.892	15.75188	10658.2
3	150.837	40.31276	10246.8
4	139.893	13.66937	9503.4
5	137.360	36.43231	9331.3
6	128.663	100.00000	8740.5
7	128.609	48.63041	8736.8
8	128.375	21.93986	8721.0
9	128.106	72.97092	8702.7
10	122.104	36.92995	8294.9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SLVNT DMSO
Processing
BF 1.22 Hz
EXREF 39.50 ppm
Plot
XS -3081.0550 Hz
XE 4072.2660 Hz
YG 3.48
OPERATOR :
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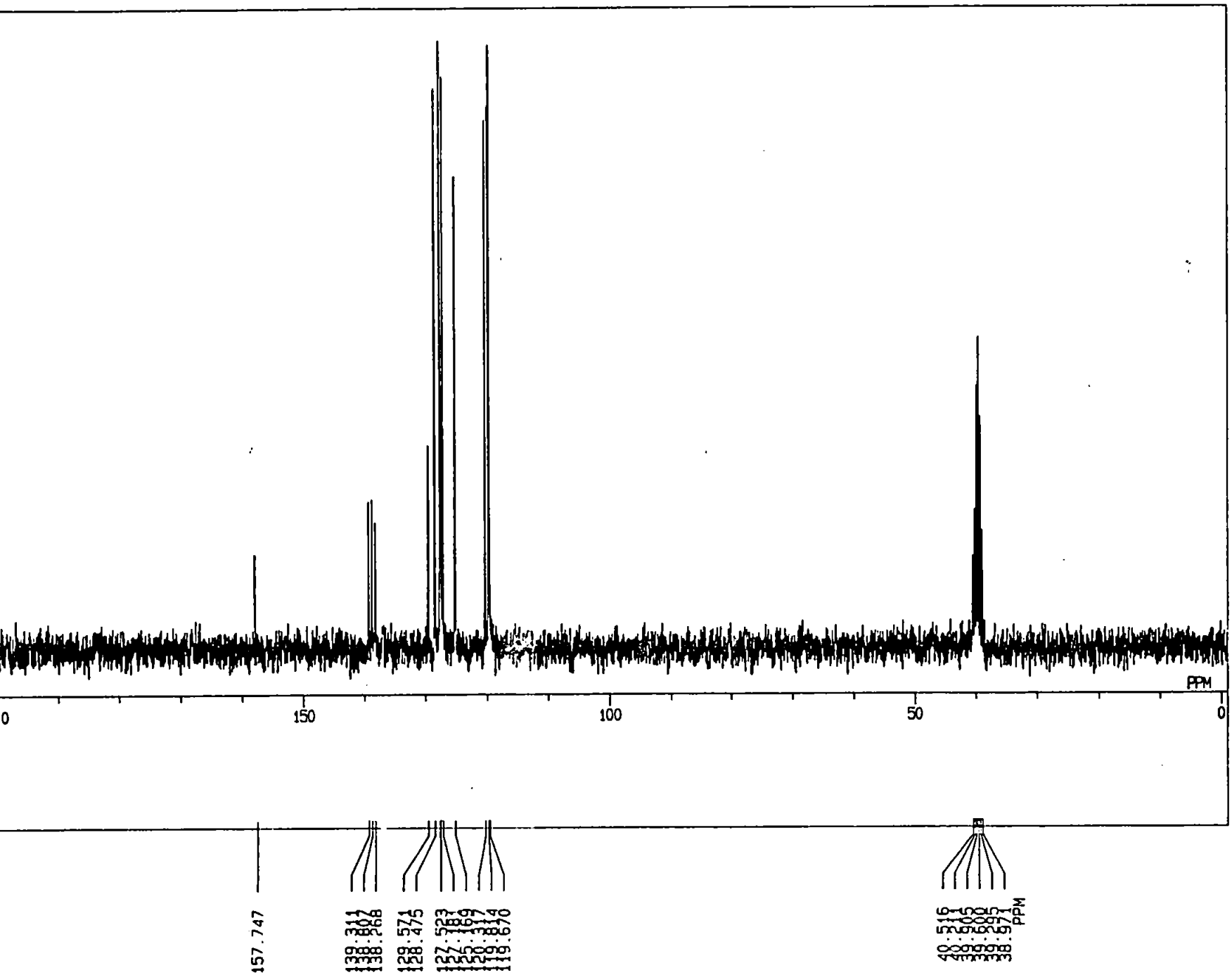
COOH
N
170
160
150
140
130
120
169.327
156.892
159.337
139.893
137.360
128.663
128.106
122.104
PPM

Appendix III.4

5H-indeno[1,2-b]pyridine-5-one hydrazone (55)

$C_{12}H_9N_3$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	157.747	18.12599	10716.3
2	139.311	24.30825	9463.8
3	138.807	24.63338	9429.7
4	138.268	20.94174	9393.0
5	129.571	33.54507	8802.2
6	128.475	92.27212	8727.8
7	127.523	85.66652	8663.1
8	127.181	94.27636	8639.9
9	125.169	77.80510	8503.2
10	120.317	87.02689	8173.6
11	119.814	89.34355	8139.4
12	119.670	99.29222	8129.6



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SLVNT	DMSO

Processing

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EXREF	39.60 ppm

Plot

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YG	2.77

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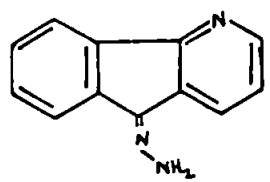

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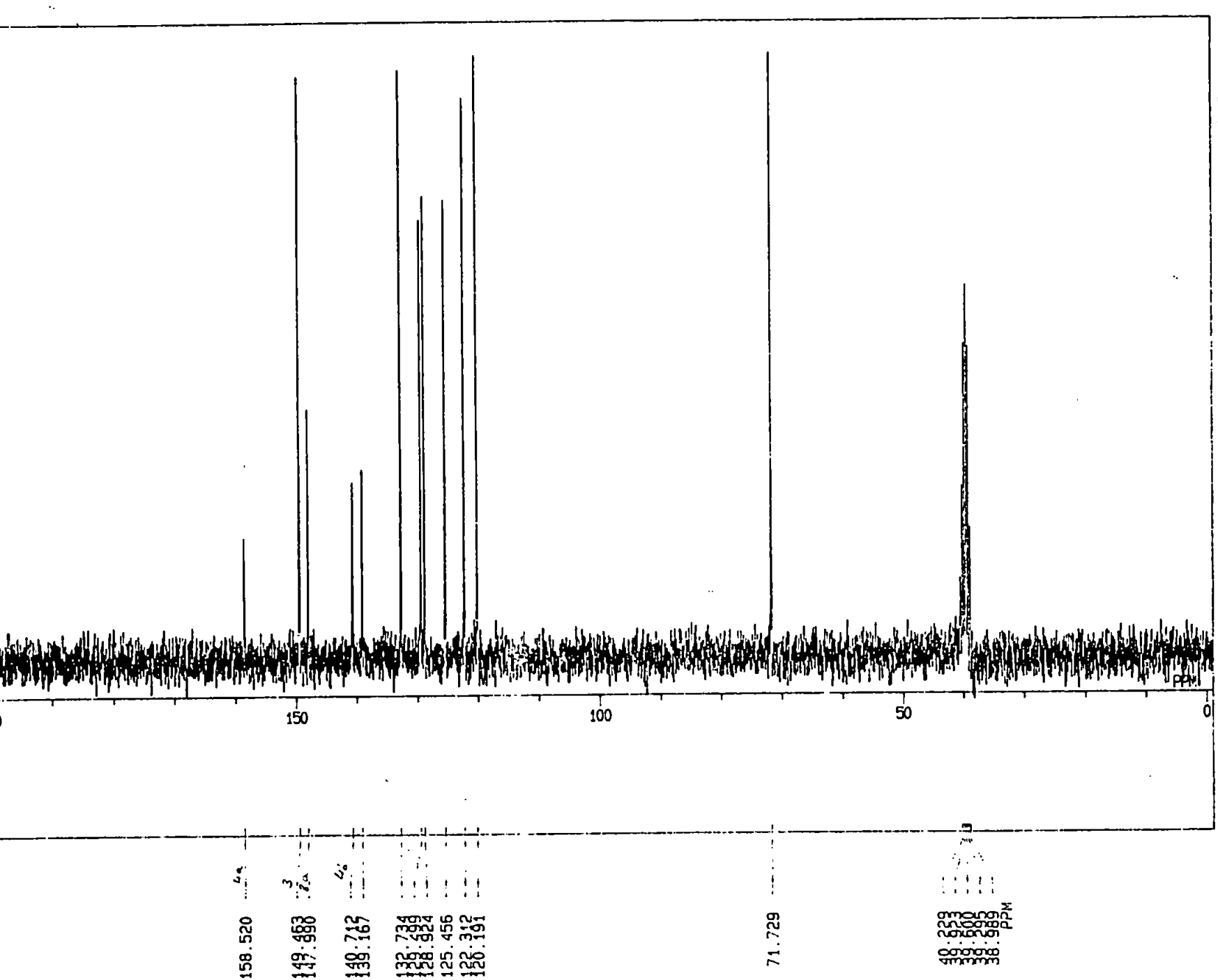
Appendix III.5

(ℓ) 5-Hydroxy-5H-indeno [1,2-b] pyridine (215)

$C_{12}H_9NO$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	158.520	19.743	10768.8
2	149.463	96.51189	10153.5
3	147.990	41.09105	10053.4
4	140.712	28.89713	9559.1
5	139.167	31.01713	9454.1
6	132.734	97.52422	9017.1
7	129.499	72.56192	8797.3
8	128.924	76.57610	8758.3
9	125.456	75.82827	8522.7
10	122.312	92.75435	8309.1
11	120.191	99.90089	8165.0
12	71.729	100.00000	4872.8



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FREQU	20000.0 Hz
SCANS	50
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	DMSO

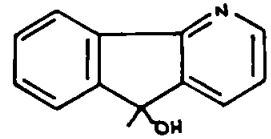
Processing

BF	1.22 Hz
EXREF	39.60 ppm

Plot

XS	25.0254 Hz
XE	13654.6200 Hz
YG	1.95

OPERATOR : _____

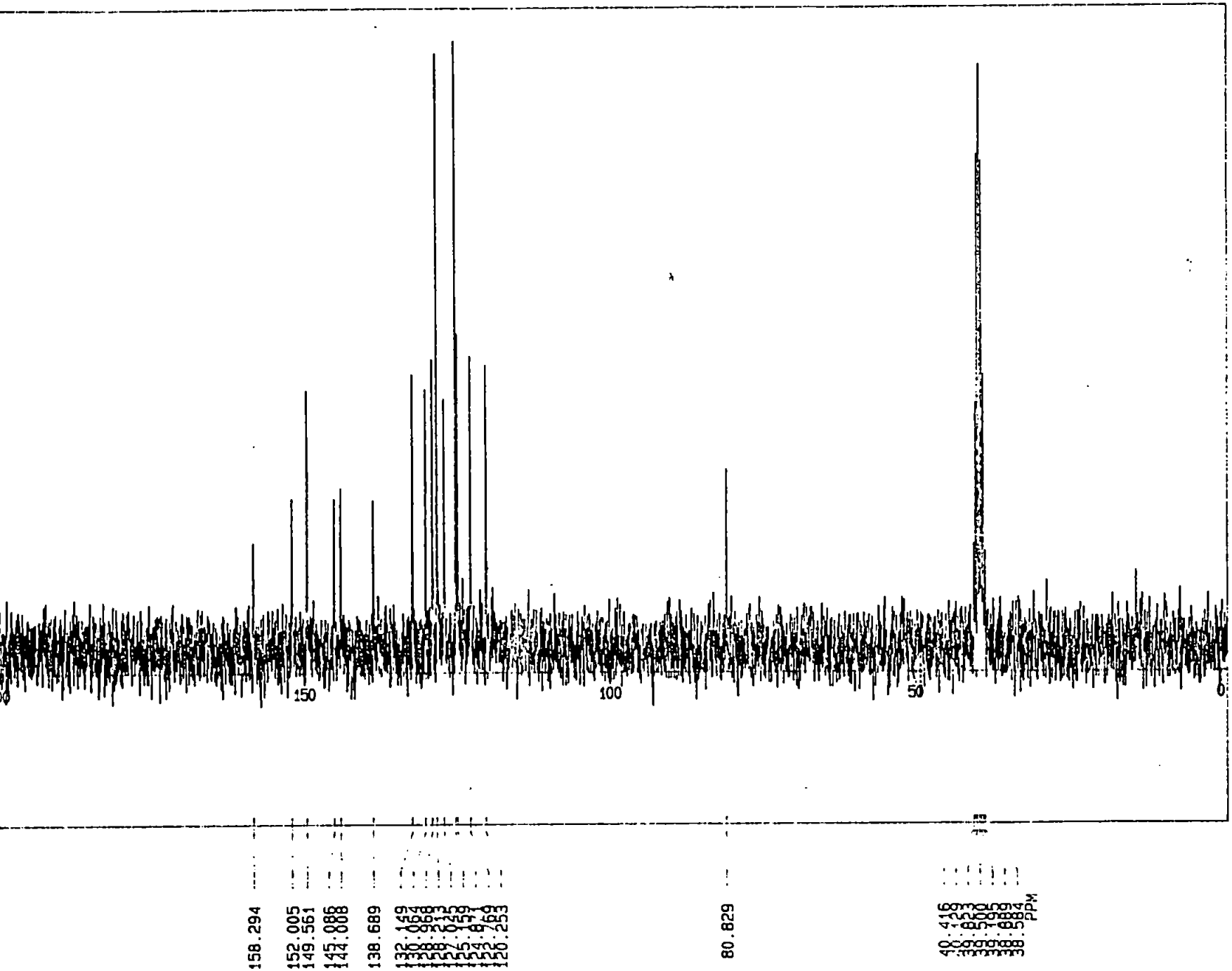


Appendix III.6

5-Phenyl-5-hydroxyindeno[1,2-b]pyridine (222)

$C_{18}H_{13}NO$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	158.294	17.221	10753.4
2	152.005	24.535	10326.2
3	149.561	42.443	10160.2
4	145.086	24.548	9856.2
5	144.008	26.282	9783.0
6	138.689	24.325	9421.7
7	132.149	45.076	8977.3
8	130.064	42.648	8835.7
9	128.968	47.524	8761.3
10	128.213	98.077	8710.0
11	127.045	40.99481	8630.6
12	125.159	100.000	8502.5
13	124.871	51.646	8482.9
14	122.769	48.075	8340.1
15	120.253	46.547	8169.2
16	80.829	29.224	5491.0
17	40.416	16.898	2745.6
18	38.584	15.636	2621.1



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ACQTM	0.819 sec
PD	1.181 sec
SLVNT	DMSO

Processing

BF	1.22 Hz
EXREF	39.50 ppm

Plot

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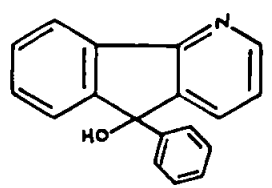
XE	13654.6200 Hz
YG	3.04

OPERATOR : _____

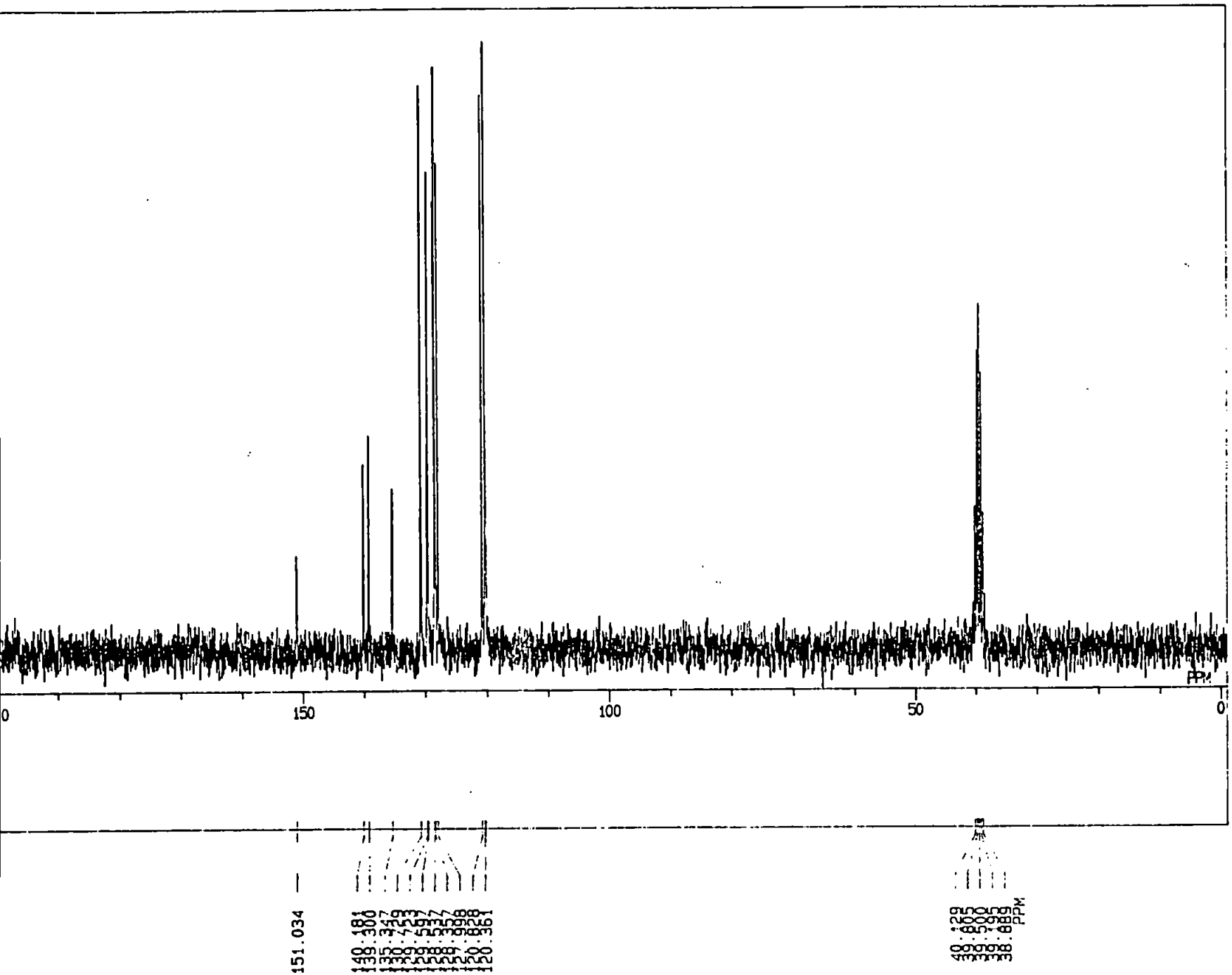


Appendix III.7

5H-indeno[1,2-b]pyridine-5-one oxime (224)

$C_{12}H_8N_2O$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	151.034	15.616	10260.3
2	140.181	30.666	9523.0
3	139.300	35.466	9463.2
4	135.347	26.575	9194.6
5	130.729	92.843	8880.9
6	129.723	33.702	8812.5
7	129.597	78.716	8804.0
8	128.537	73.774	8732.0
9	128.357	95.896	8719.7
10	127.998	80.174	8695.3
11	120.828	91.264	8202.3
12	120.361	100.000	8176.5



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SCANS	50
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	DMSO

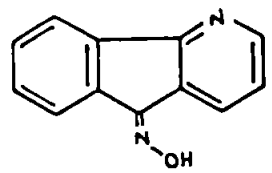
Processing

BF	1.22 Hz
EXREF	39.50 ppm

Plot

XS	15.7910 Hz
XE	13654.6200 Hz
YG	3.11

OPERATOR : _____



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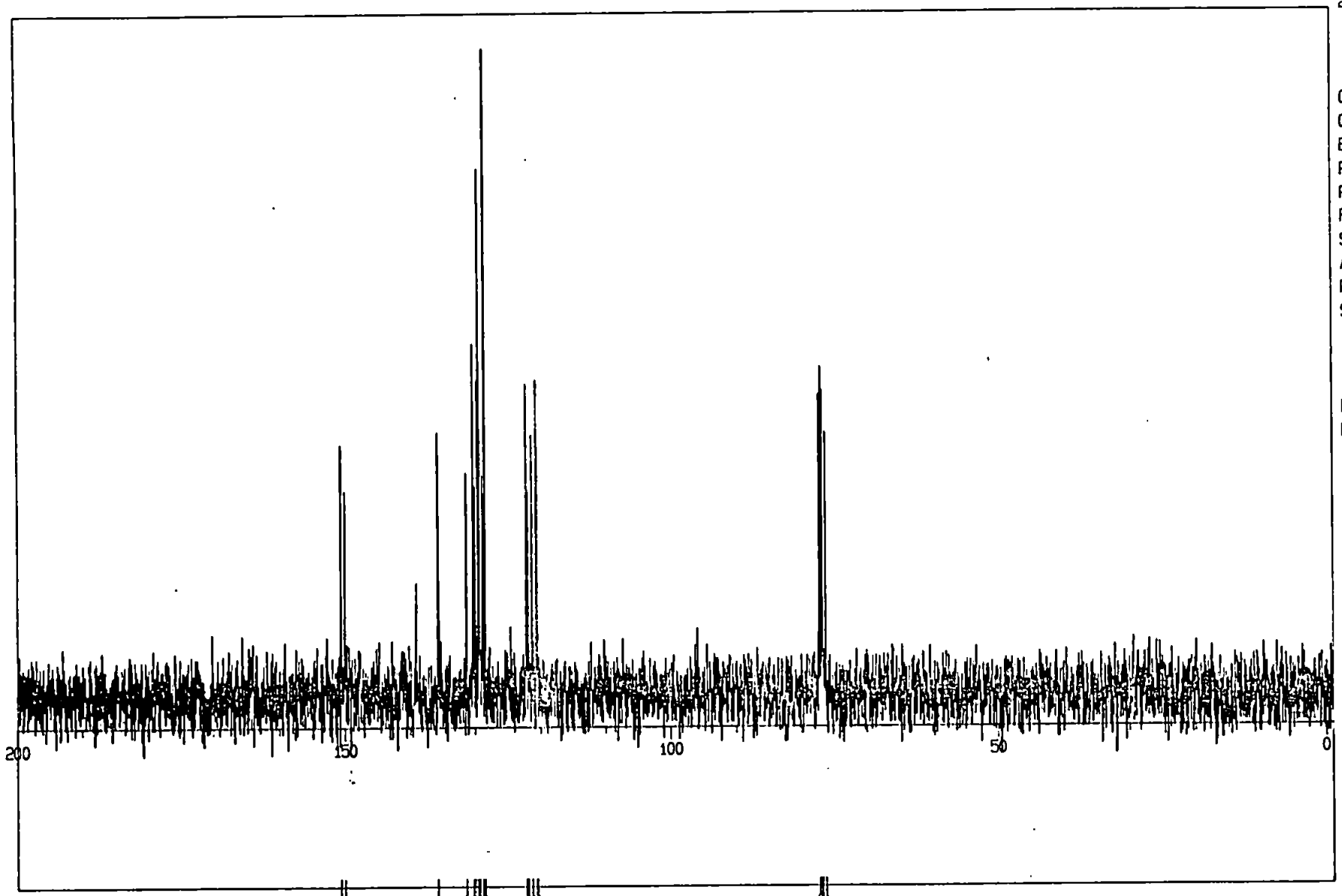
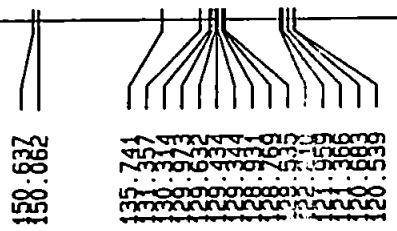
Appendix III.8

5H-indeno[1,2-b]pyridin-5-one 4-chlorobenzyloxime (225)

$C_{19}H_{13}N_2OCl$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	150.637	38.87389	10233.3
2	150.062	31.79236	10194.3
	138.0		
3	135.741	40.76198	9221.4
4	131.357	34.66195	8923.5
5	130.314	54.45968	8852.7
6	129.973	32.48300	8829.5
7	129.632	48.78187	8806.3
8	129.434	81.54029	8792.9
9	129.344	49.21246	8786.8
10	128.931	34.10738	8758.7
11	128.769	31.30946	8747.7
12	128.535	100.00000	8731.8
13	122.210	48.17536	8302.2
14	121.959	31.88399	8285.1
15	121.366	40.32071	8244.8
16	120.683	48.88435	8198.4
17	120.539	38.35715	8188.6
18	76.964	50.66137	5228.4





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SCANS	50
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

Processing

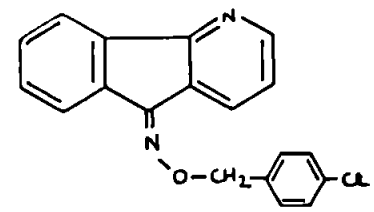
BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	53.5293 Hz
XE	13654.6100 Hz
YG	2.60

360

OPERATOR : _____

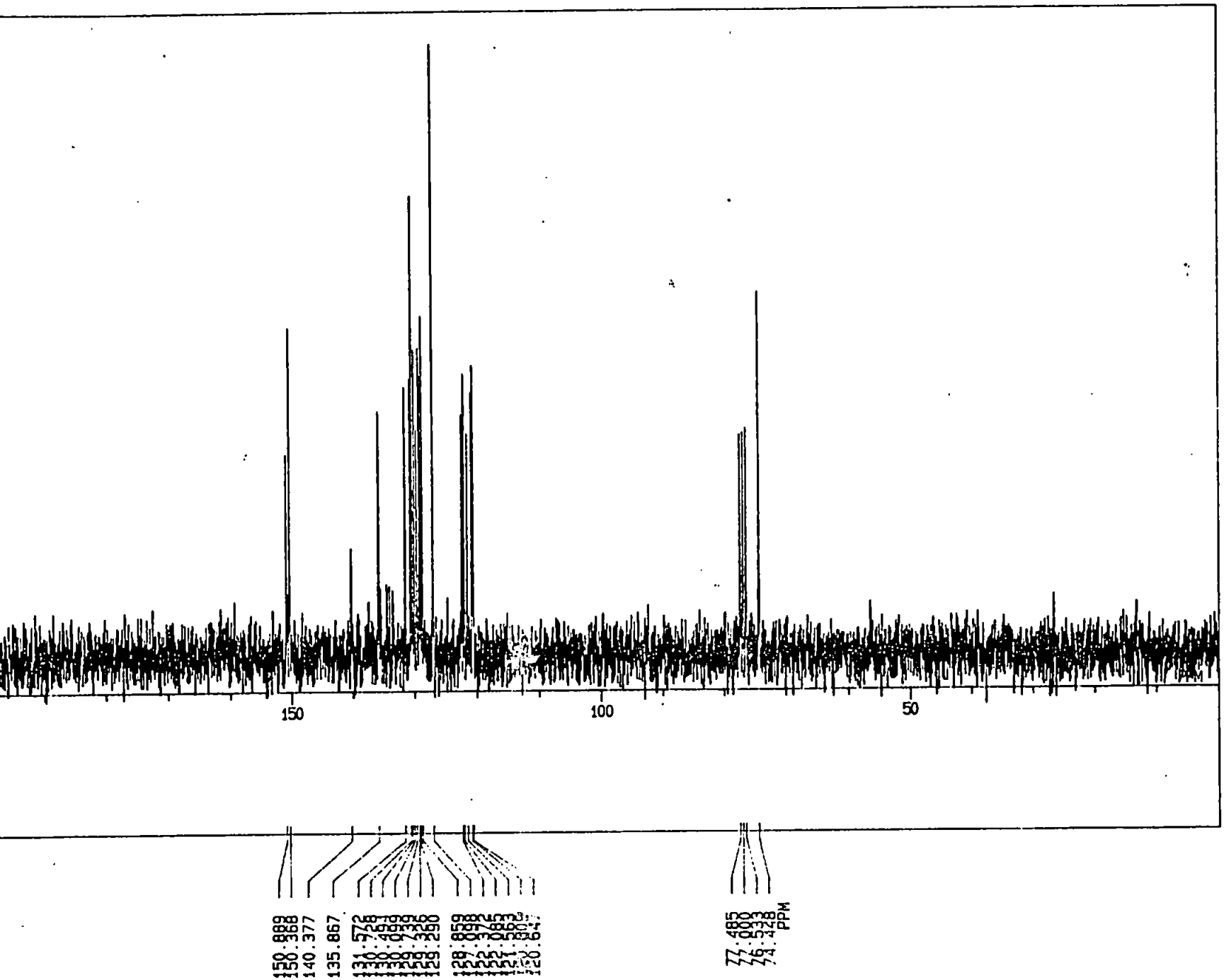


Appendix III.9

5H-indeno[1,2-b]pyridine-5-one 2,4-dichlorobenzyloxime **(226)**

$C_{19}H_{12}N_2OCl_2$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	150.889	32.73276	10250.4
2	150.368	53.57168	10215.0
3	140.377	17.27290	9536.3
4	135.867	39.76220	9229.9
5	131.572	43.74437	8938.1
6	130.728	45.10150	8880.8
7	130.494	75.15963	8864.9
8	130.099	49.82367	8838.0
9	129.739	36.76849	8813.6
10	129.326	50.19113	8785.6
11	129.290	47.34994	8783.1
12	128.859	55.39841	8753.8
13	127.098	100.00000	8634.2
14	122.372	39.23608	8313.1
15	122.085	45.92479	8293.6
16	121.563	35.96256	8258.2
17	120.809	42.78948	8206.9
18	120.647	47.25890	8196.0
19	74.448	59.05801	5057.5



EX270

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FREQU	20000.0 Hz
SCANS	16
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

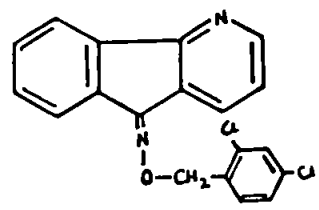
Processing

BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	29.3281 Hz
XE	13586.6800 Hz
YG	2.28

OPERATOR : _____



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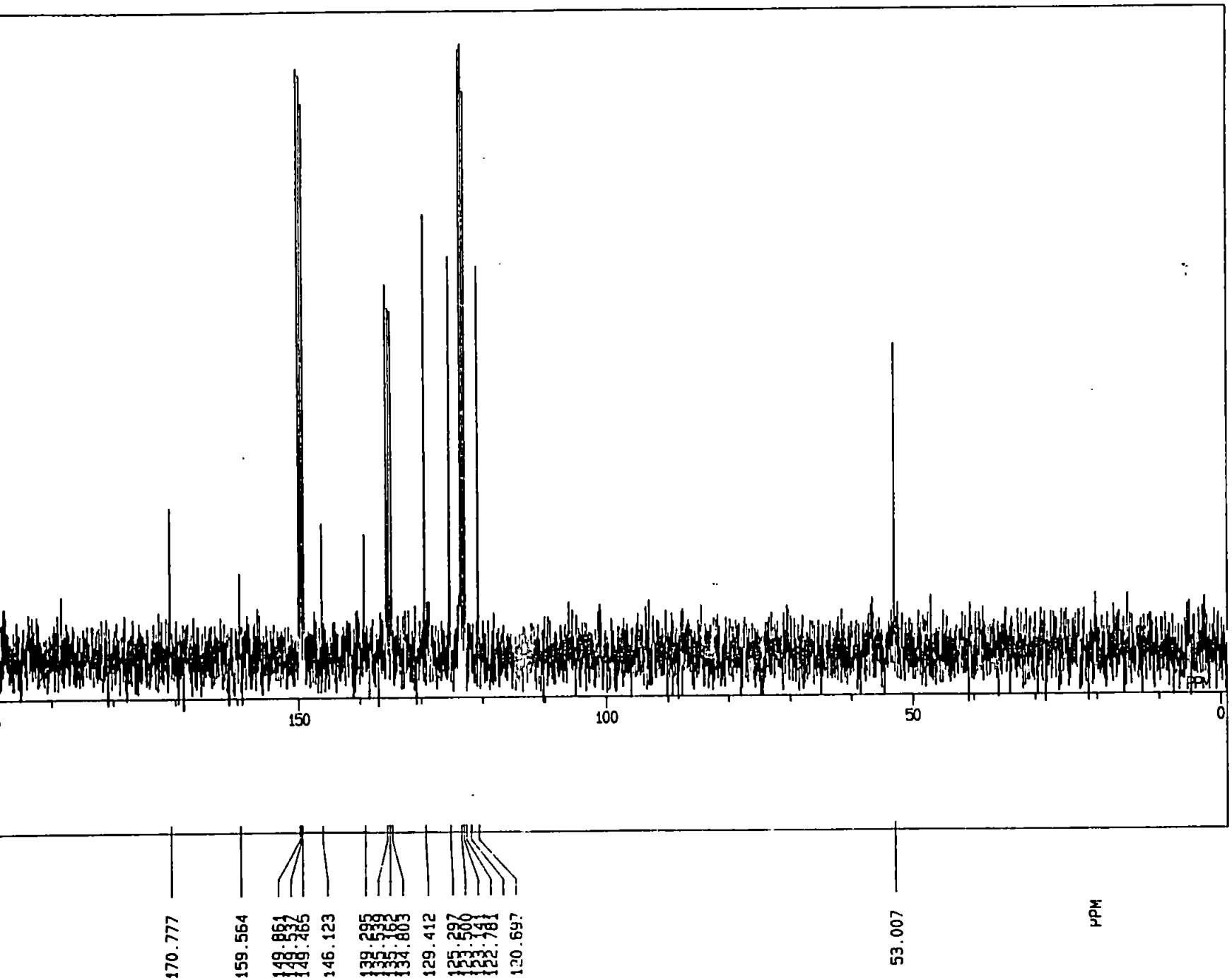
Appendix III.10

5-Acetamido-5H-indeno[1,2-b]pyridine (230)

$C_{14}H_{12}N_2O$ (C_5D_5N)

No	PPM	INT(%)	FREQ(Hz)	
1	170.777	24.09133	11601.5	
2	159.564	13.28267	10839.7	
3	149.861	96.09024	10180.6	(pyridine)
4	149.537	64.48449	10158.6	
5	149.465	95.05297	10153.7	
6	146.123	21.41676	9926.7	
7	139.295	19.57439..	9462.8	
8	135.539	60.65404	9207.7	(pyridine)
9	135.162	56.65191	9182.0	
10	134.803	56.25333	9157.6	
11	129.412	72.09106	8791.4	
12	125.297	65.23098	8511.9	
13	123.500	99.06312	8389.8	(pyridine)
14	123.141	100.00000	8365.4	
15	122.781	92.29408	8341.0	
16	120.697	63.62191	8199.4	
17	53.007	50.46922	3601.0	



20-JAN-93 10:19:28

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	ECM
POINT	32768
PW1	5.0 us
FREQU	20000.0 Hz
SCANS	50
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	C5D5N

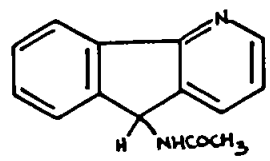
Processing

BF	1.22 Hz
EXREF	123.50 ppm

Plot

XS	-41.9595 Hz
XE	13654.6300 Hz
YG	2.89

OPERATOR : _____



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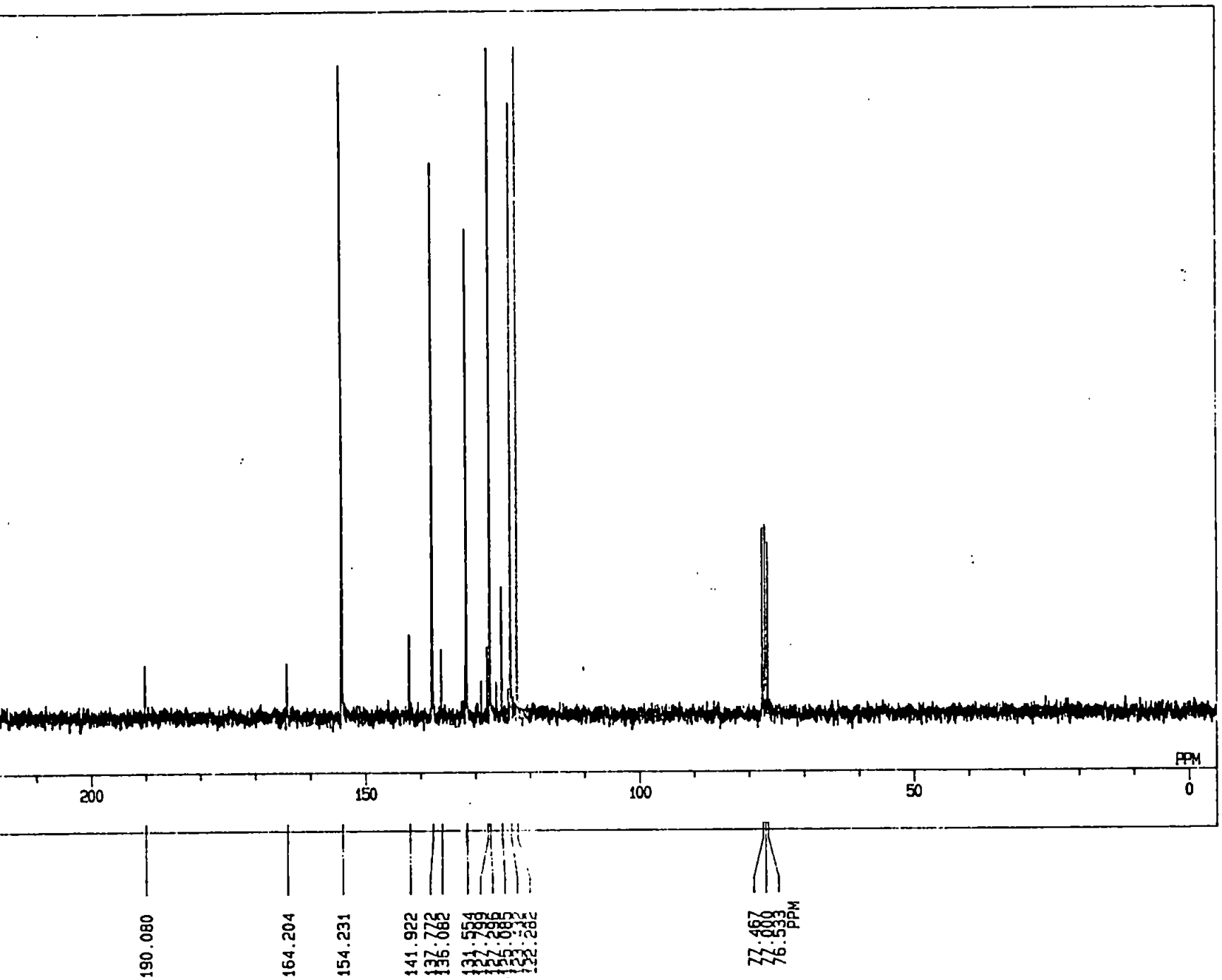
Appendix 1II.11

7-Bromo-5H-indeno[1,2-b]pyridine-5-one(233)

$C_{12}H_6NOBr$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	190.080	7.747	12912.8
2	164.204	7.931	11154.9
3	154.231	97.415	10477.5
4	141.922	12.128	9641.3
5	137.772	82.858	9359.3
6	136.082	9.906	9244.5
7	131.554	72.842	8936.9
8	127.799	10.209	8681.8
9	127.296	99.906	8647.6
10	125.085	19.241	8497.5
11	123.432	91.721	8385.2
12	122.282	100.000	8307.0



EX270

20-JUN-91 13:27:15

Accumulation

OBNUC	13C
OFA	67.80 MHz
EXMOD	BCM
POINT	32768
PW1	5.5 us
FREQU	20000.0 Hz
SCANS	194
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

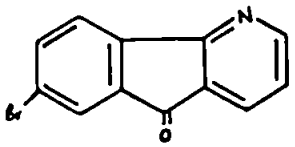
Processing

BF	1.50 Hz
EXREF	77.00 ppm

Plot

XS	-477.7290 Hz
XE	15285.0100 Hz
YG	3.33

OPERATOR : _____



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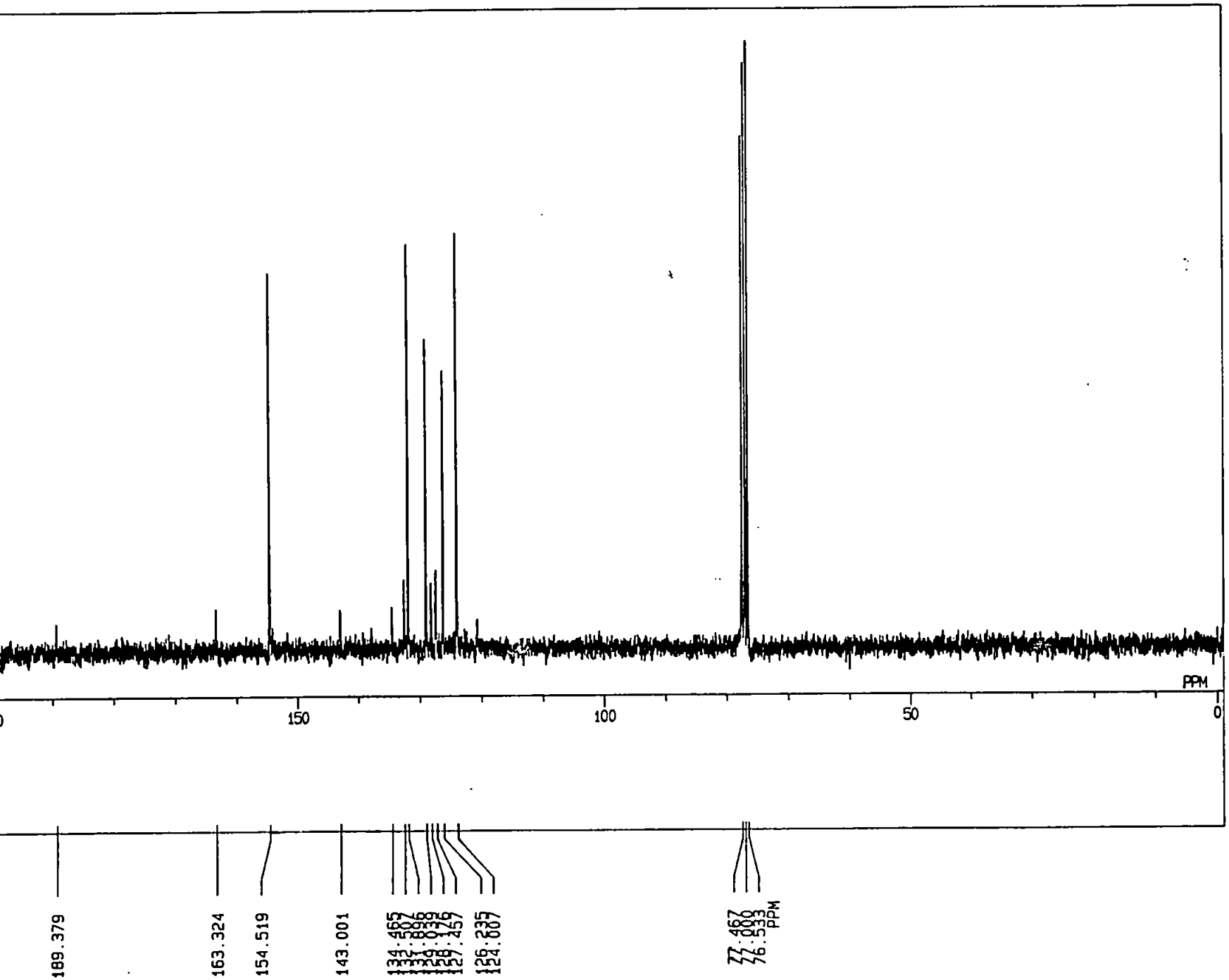
Appendix III.12

7,9-Dibromo-5H-indeno[1,2-b]pyridine-5-one (234)

$C_{12}H_5NOBr_2$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	189.379	4.82522	12865.1
2	163.324	7.09820	11095.1
3	154.519	62.28356	10497.0
4	143.001	6.80180	9714.5
5	134.465	7.21734	9134.7
6	132.507	11.78277	9001.6
7	131.896	66.94321	8960.1
8	129.039	51.30193	8766.0
9	128.176	11.20362	8707.4
10	127.457	13.33478	8658.6
11	126.235	46.20353	8575.6
12	124.007	68.67352	8424.2



25-NOV-92 16:14:05

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	BCM
POINT	32768
PW1	5.0 us
FREQU	20000.0 Hz
SCANS	2500
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

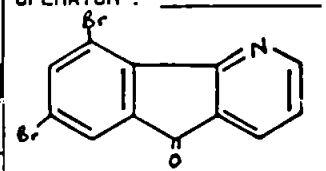
Processing

BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	69.3989 Hz
XE	13654.6100 Hz
YG	3.50

OPERATOR : _____



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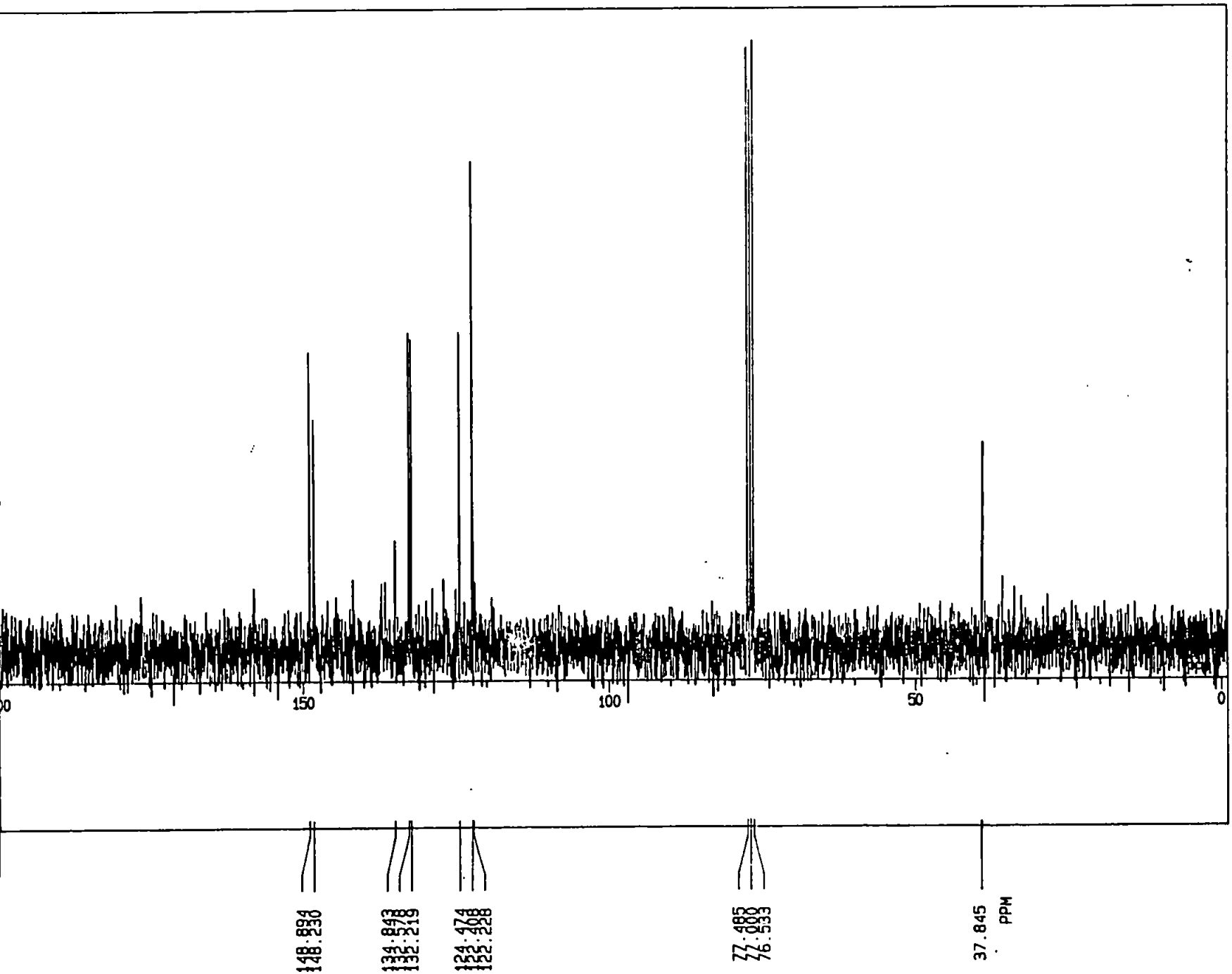
Appendix III.13

Tetrabromo-5H-indeno[1,2-b]pyridine (237)

$C_{12}H_5NBr_4$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	148.894	49.09244	10114.9
2	148.230	38.03317	10069.7
3	134.843	17.96338	9160.3
4	132.578	52.14948	9006.5
5	132.219	51.07998	8982.1
6	124.474	52.22791	8456.0
7	122.408	80.44189	8315.6
8	122.228	17.75626	8303.4
9	37.845	39.01187	2571.0



21-APR-93 13:33:01

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	BCM
POINT	32768
PW1	5.0 us
FREQU	20000.0 Hz
SCANS	256
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

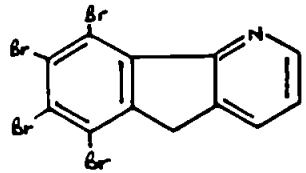
Processing

BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	68.1782 Hz
XE	13654.6100 Hz
YG	2.24

OPERATOR : _____



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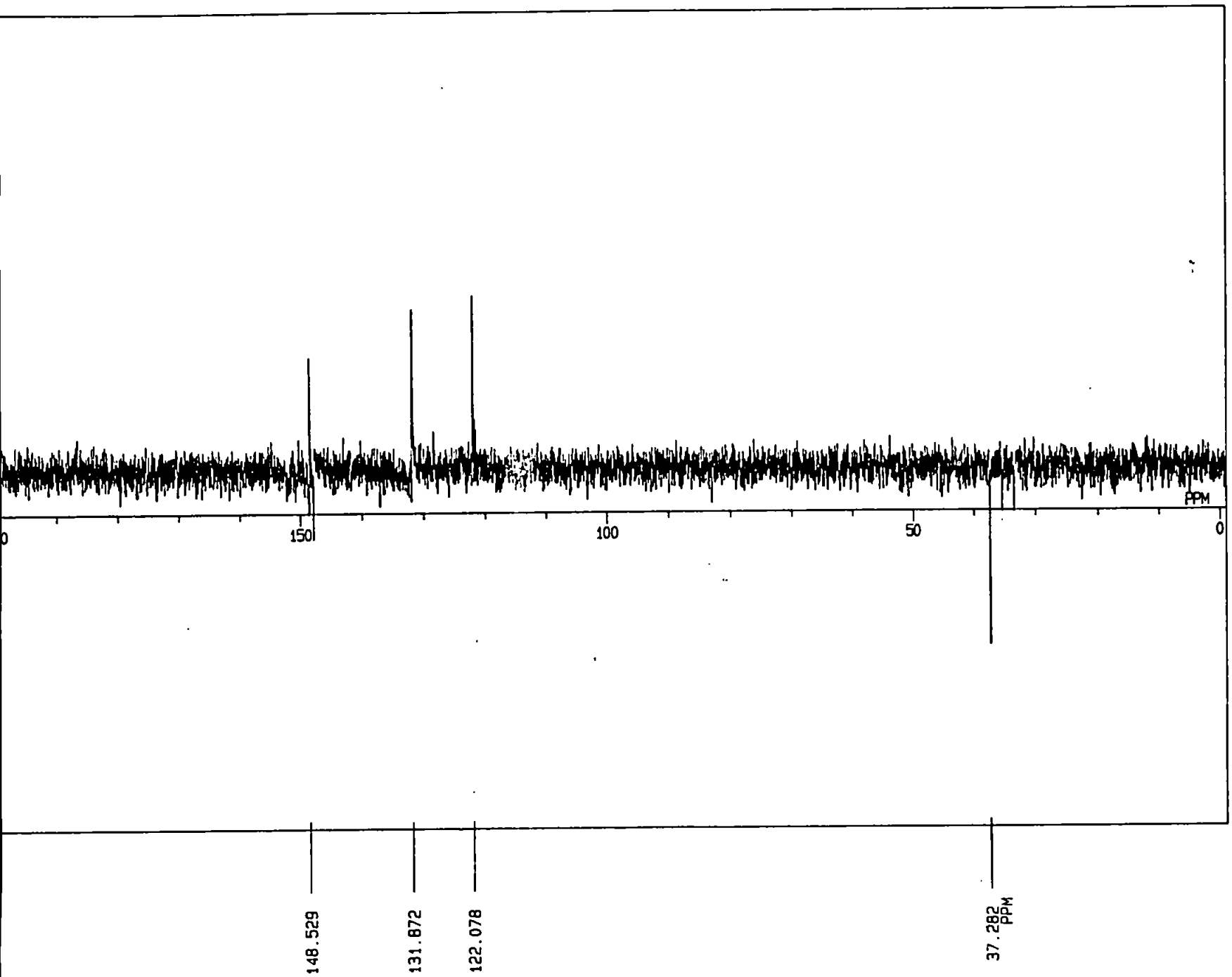
Appendix III.14

DEPT Measurement of Tetrabromo-5H-indeno[1,2-b]pyridine (237)

$C_{12}H_5NBr_4$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	148.529	+62.75336	10090.1
2	131.872	+89.43915	8958.5
3	122.078	+96.68095	8293.2
4	37.282	-100.0000	2532.7



21-APR-93 13:50:36

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	DEPT
POINT	32768
PW1	10.0 us
FREQU	20000.0 Hz
SCANS	125
ACQTM	0.819 sec
PD	4.724 sec
SLVNT	CDCL3

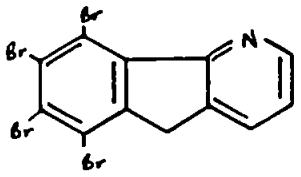
Processing

BF	1.22 Hz
EXREF	101.36 ppm

Plot

XS	44.5688 Hz
XE	13654.6100 Hz
YG	1.00

OPERATOR : _____



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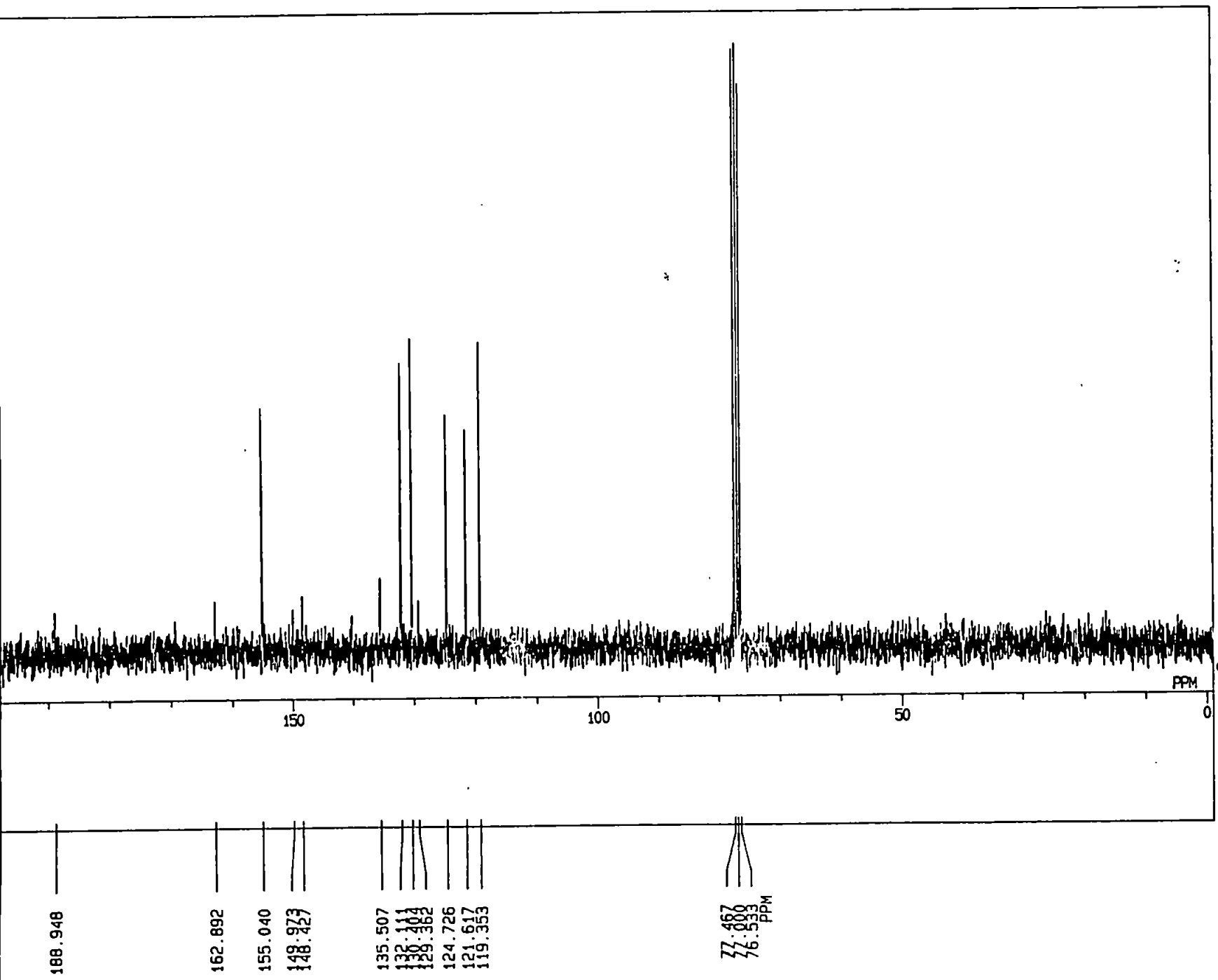
Appendix III.15

7-nitro-5H-indeno[1,2-b]pyridine-5-one (238)

$C_{12}H_6N_2O_3$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	188.948	6.70354	12835.9
2	162.892	8.23739	11065.8
3	155.040	40.20445	10532.4
4	149.973	6.70633	10188.1
5	148.427	8.99141	10083.2
6	135.507	11.89534	9205.5
7	132.111	47.53668	8974.8
8	130.404	51.64404	8858.8
9	129.362	8.05518	8788.0
10	124.726	38.87501	8473.1
11	121.617	36.34389	8261.9
12	119.353	50.85040	8108.1



21-APR-93 11:08:42

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	BCM
POINT	32768
PW1	4.1 us
FREQU	20000.0 Hz
SCANS	250
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

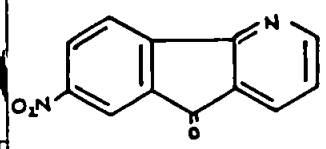
Processing

BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	68.1782 Hz
XE	13654.6100 Hz
YG	2.68

OPERATOR : _____



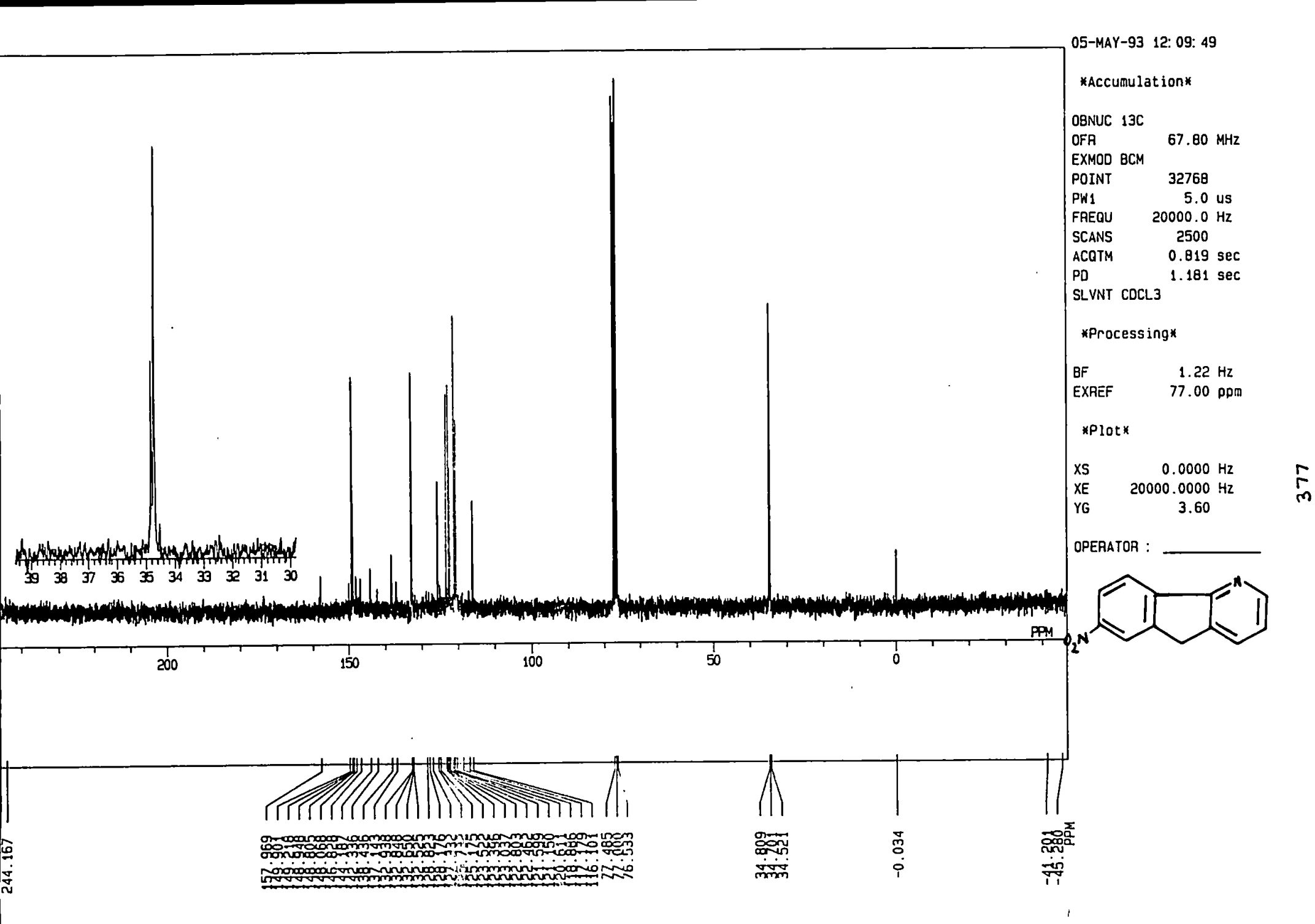
Appendix III.16

7-nitro-5H-indeno[1,2-b]pyridine (239)

$C_{12}H_8N_2O_2$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	244.167	3.27745	16587.1
2	157.969	6.61162	10731.4
3	149.901	5.27203	10183.3
4	149.218	44.16140	10136.9
5	148.948	20.32632	10118.6
6	148.805	3.73706	10108.8
7	148.068	6.47240	10058.8
8	146.828	6.07089	9974.5
9	144.187	7.92572	9795.1
10	142.336	4.08178	9669.3
11	138.436	10.51240	9404.5
12	137.143	5.42631	9316.6
13	132.938	44.89068	9030.9
14	132.848	25.76986	9024.8
15	132.650	3.12170	9011.4
16	132.525	3.12880	9002.8
17	128.823	3.53627	8751.4
18	128.176	3.34138	8707.4
19	127.332	3.15120	8650.1
20	125.732	24.27728	8541.4
21	125.175	4.64217	8503.6
22	123.522	25.12111	8391.3
23	123.396	40.89267	8382.7
24	123.037	3.02222	8358.3
25	122.803	42.58369	8342.4

No	PPM	INT(%)	FREQ(Hz)
26	122.462	26.86157	8319.2
27	121.599	3.07401	8260.7
28	121.150	55.62733	8230.1
29	120.611	35.90575	8193.5
30	118.886	3.25457	8076.3
31	117.179	3.64136	7960.4
32	116.101	20.62802	7887.1
33	34.809	27.24929	2364.7
34	34.701	57.50012	2357.3
35	34.521	4.29815	2345.1

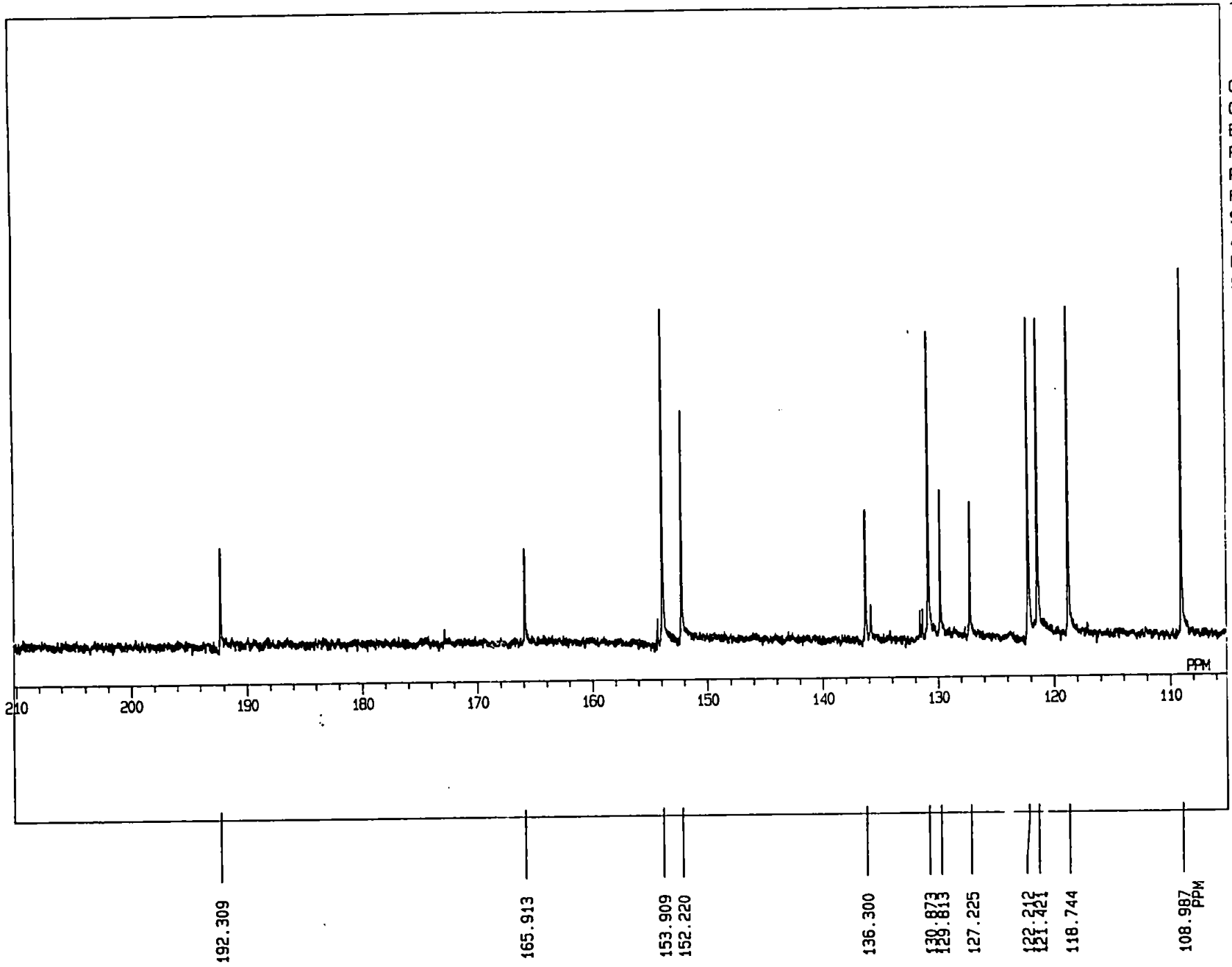

05-MAY-93 12: 09: 49
Accumulation
OBNUC 13C
OFR 67.80 MHz
EXMOD BCM
POINT 32768
PW1 5.0 us
FREQU 20000.0 Hz
SCANS 2500
ACQTM 0.819 sec
PD 1.181 sec
SLVNT CDCL3
Processing
BF 1.22 Hz
EXREF 77.00 ppm
Plot
XS 0.0000 Hz
XE 20000.0000 Hz
YG 3.60
OPERATOR :
377
39 38 37 36 35 34 33 32 31 30
200 150 100 50 0
PPM
244.167
157.969
149.901
148.218
34.809
34.521
-0.034
-41.280
-45.280
PPM

Appendix III.17

7-amino-5H-indeno[1,2-b]pyridine-5-one (241)

$C_{12}H_8N_2O$ (DMSO)

No	PPM	INT(%)	FREQ(Hz)
1	192.309	26.19566	13064.2
2	165.913	25.25807	11271.0
3	153.909	90.34520	10455.6
4	152.220	63.27037	10340.8
5	136.300	34.69484	9259.3
6	130.873	83.45020	8890.6
7	129.813	39.86926	8818.6
8	127.225	36.58674	8642.8
9	122.212	86.98660	8302.3
10	121.421	86.68516	8248.6
11	118.744	89.87518	8066.7
12	108.987	100.00000	7403.8


15-JAN-93 12:58:38
Accumulation
OBNUC 13C
OFR 67.80 MHz
EXMOD BCM
POINT 32768
PW1 5.0 us
FREQU 20000.0 Hz
SCANS 2500
ACQTM 0.819 sec
PD 1.181 sec
SLVNT DMSO
Processing
BF 1.22 Hz
EXREF 39.50 ppm
Plot
XS -3925.7810 Hz
XE 7138.6720 Hz
YG 2.22
OPERATOR :
PPM
210
200
190
180
170
160
150
140
130
120
110
192.309
165.913
153.909
152.220
136.300
130.873
129.813
127.225
122.212
121.421
118.744
108.987
PPM
H2N
N
O

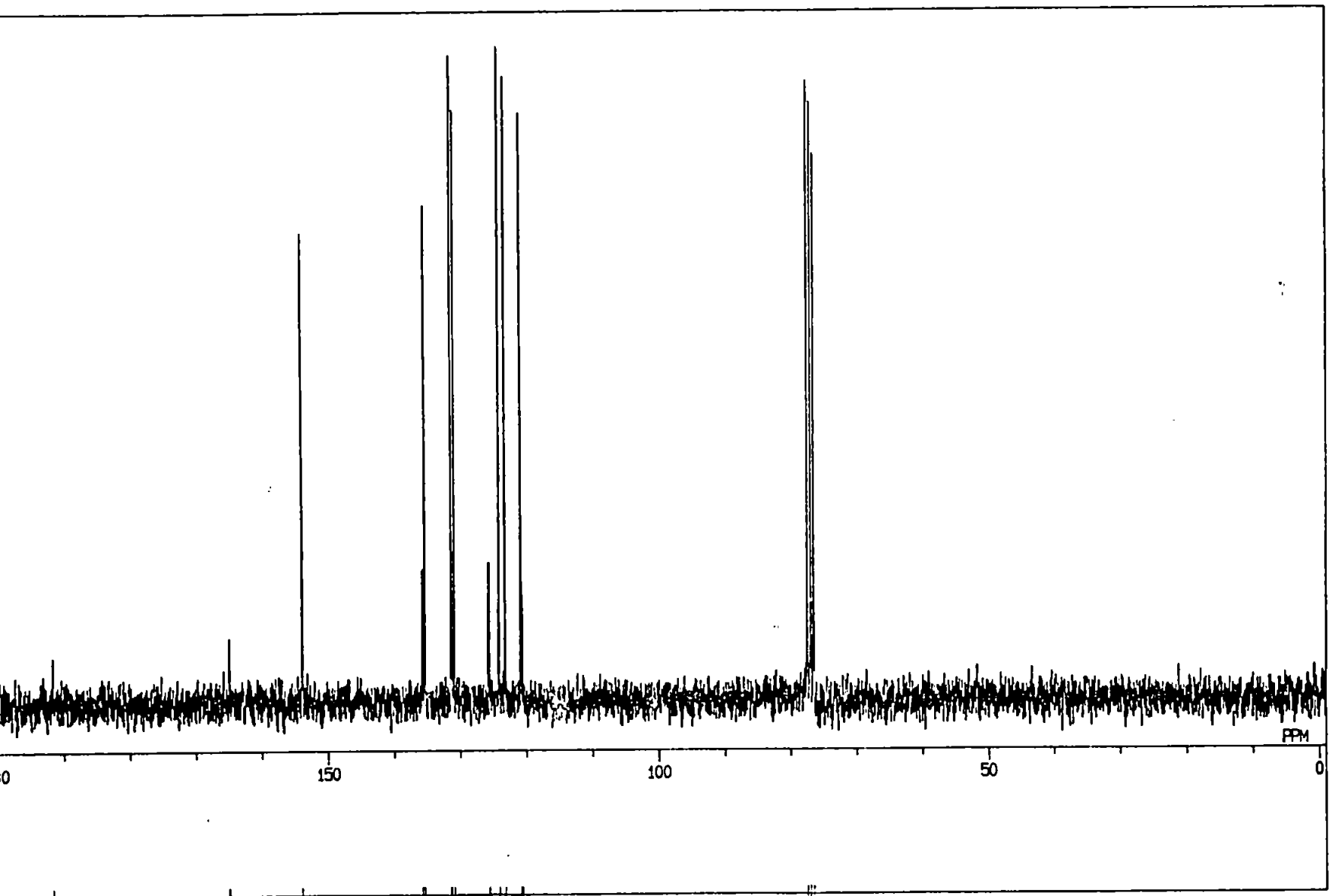
379

Appendix III.18

5H-indeno[1,2-b]pyridine-5-one N-oxide (249)

$C_{12}H_7NO_2$ ($CDCl_3$)

No	PPM	INT(%)	FREQ(Hz)
1	191.733	6.84895	13025.1
2	164.977	9.69238	11207.4
3	153.962	71.69741	10459.1
4	135.687	20.10459	9217.7
5	135.328	75.80941	9193.3
6	131.446	26.15831	8929.6
7	130.961	90.38587	8896.6
8	125.606	21.18670	8532.9
9	124.133	100.00000	8432.8
10	123.253	95.56190	8373.0
11	120.899	89.92075	8213.0
12	120.683	16.08685	8198.4



03-APR-92 09: 41: 53

Accumulation

OBNUC	13C
OFR	67.80 MHz
EXMOD	BCM
POINT	32768
PW1	5.0 us
FREQU	20000.0 Hz
SCANS	500
ACQTM	0.819 sec
PD	1.181 sec
SLVNT	CDCL3

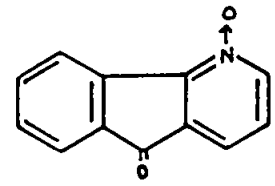
Processing

BF	1.22 Hz
EXREF	77.00 ppm

Plot

XS	65.7368 Hz
XE	13654.6100 Hz
YG	3.09

OPERATOR : _____



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Appendix IV. Developing Solvents for Thin Layer Chromatography.

Unless otherwise stated, the developing solvent used was 50/50 petroleum spirit (40-60) / ethyl acetate.

Key	Solvent (v/v%)
1a	Chloroform (100%)
1b	Dichloromethane (100%)
1c	Ethyl acetate (100%)